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SHORT COMMUNICATION

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Layered assemblies composed of sulfonated cyclodextrin and poly(allylamine)

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Abstract Layered assemblies containing cyclodextrin (CD) have been prepared by layer-by-layer deposition of poly(allylamine) and sulfonated α-CD or β-CD on a solid surface. A quartz crystal microbalance study revealed that α-CD and β-CD form multilayers in the films upon each deposition. The sulfonated-α-CD-containing film bound methyl orange (MO) by forming an inclusion complex, resulting in the isolation of MO as a monomer in the film, whereas MO formed aggregates in the sulfonated-β-CD and CD-free films.

Keywords Layered assembly · Cyclodextrin · Layered thin film · Layer-by-layer deposition · Methyl orange

Introduction

Cyclodextrin (CD)-containing thin films are attracting much attention because of their possible applications to detection and separation of organic compounds through a host–guest complexation. CD-containing films have been prepared by casting a CD–lipid mixed solution [1], forming a self-assembled monolayer of thiol-modified CD [2], and deposition and cross-linking of CD polymers [3]. Recently, Yang et al. [4] reported multilayer films containing sulfonated CD (s-CD), which were prepared by an alternate adsorption of negatively charged s-CD and polycation [4]. However, the s-CD multilayer films have not been fully characterized and the films, unfortunately, showed poor sensitivity toward gases such as halogenated hydrocarbons and toluene. In this context, we have reported that CD-containing multilayer films can be prepared by layer-by-layer deposition of a CD dimer and ferrocene-modified polymers [5]. In the CD-dimer-containing films, however, the binding activity of the CD dimer was practically masked because the CD cavity was occupied by ferrocene residues in the film (i.e., the films were constructed through host–guest interactions between the CD dimer and ferrocene moieties in the polymer). If the CD cavity were available in the film, it would be possible to make the film functional by modifying the film with various kinds of guest molecules. The present paper reports a preliminary result on the binding property of layered assemblies containing sulfonated α-CD (s-α-CD) and β-CD (s-β-CD).

Experimental

The layered assemblies containing s-α-CD or s-β-CD were prepared on the surface of a platinum-coated quartz resonator (9 MHz, surface area 0.4 cm^2) to monitor the deposition of the s-CDs by a quartz crystal microbalance (QCM). The layered assemblies were constructed according to the reported procedure [6, 7]. Briefly, the quartz resonator was immersed in a solution of 0.1 mg ml^{-1} poly(allylamine) hydrochloride (PAH, Nittobo Co., Japan, molecular weight about 10,000) for 30 min at about 20 °C to deposit the first PAH layer. After being rinsed in water for 10 min, the PAH-adsorbed quartz resonator was immersed in 0.1 mg ml^{-1} solution of s-α-CD or s-β-CD (Aldrich Chemical Co., USA, 8–9 and 12–14 primary and secondary hydroxyl groups in α-CD and β-CD, respectively, are sulfonated) for 30 min to deposit the s-CD through electrostatic force of attraction. The deposition was repeated to prepare the multilayer films composed of a desired number of layers. The procedure for forming the multilayer assembly is illustrated schematically in Fig. 1. A phosphate buffered saline (PBS) containing s-CD or PAH was employed as a bathing solution in order to prepare the multilayer films. The PBS contains 0.2 g l^{-1} KCl, 0.2 g l^{-1} KH_2PO_4, 1.15 g l^{-1} Na_2HPO4, and 8.0 g l^{-1} NaCl (the pH was adjusted at 5.4 by adding HCl). The multilayer film-coated resonator was dried in air and the resonance frequency was measured after each deposition to monitor the loading of s-CD and PAH.

The s-α-CD and s-β-CD multilayer films were prepared on the surface of a quartz slide (5×1×0.1 cm) in a similar manner. The multilayer film-coated slide was immersed in 1×10^{-4} M methyl orange (MO) solution (10 mM Tris-HCl buffer, pH 7.5) for 12 h and UV–vis absorption spectra of the slide were measured after it had been rinsed in the buffer.

Results and discussion

The changes in the resonance frequency, ΔF, upon deposition of s-CD and PAH are shown in Fig. 2 as a function of the number of layers (the odd layer numbers show the deposition of PAH, and the even numbers correspond to the deposition of s-CD). The $-\Delta F$ value increased upon deposition of both PAH and s-CDs, suggesting that PAH and s-CD layers were grown as illustrated in Fig. 1. The loading of s-α-CD in the film was estimated on the basis of the fact that, for the 9-MHz QCM used, the adsorption of 1 ng of substance induces a −0.91-Hz change in ΔF [8]. Assuming that s-α-CD forms a closely packed monomolecular layer in each layer of the film, the density of s-α-CD in each layer is calculated to be $(1.3\pm0.2)\times10^{-10}$ mol cm^{-2}, depending on the orientation of the s-α-CD molecule. In other words, $-\Delta F$ should increase (80 ± 12) Hz per layer for the monomolecular deposition. The slope of the graph in Fig. 2, curve (a) is 650 ± 200 Hz per layer for the first 2–5 layers and 2,000 ± 500 Hz per layer for layers 6–10, suggesting that the loading of s-α-CD is 8 times and 25 times higher, respectively, than that calculated for the monomolecular deposition. On the other hand, the slope of the graph for the s-β-CD film is 470 ± 100 Hz, which corresponds to a 5-times higher value than that calculated for the monomolecular deposition.

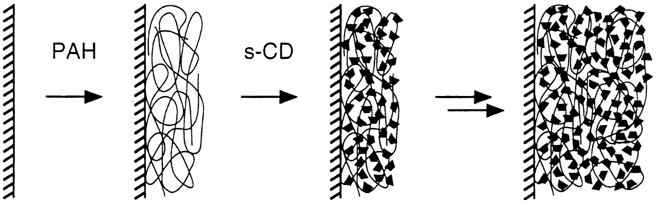

Fig. 1 Layer-by-layer deposition of poly(allylamine) hydrochloride (*PAH*) and sulfonated cyclodextrin (*s-CD*) on a solid surface

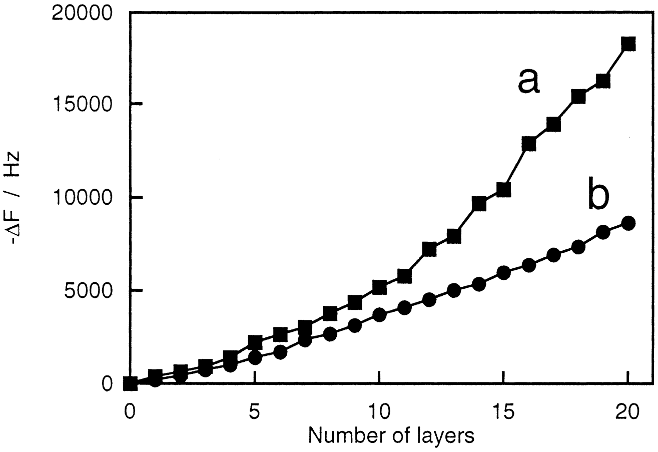

Fig. 2 Typical quartz crystal microbalance frequency changes for the formation of $(PAH–s-\alpha CD)_n$ (*a*) and $(PAH–s-\beta-CD)_n$ multilayer films (*b*). The odd layer numbers shows the deposition of PAH, and the even numbers correspond to the deposition of s-α-CD or s-β-CD

The formation of a multilayer of s-CDs upon each deposition may be rationalized by taking into account the molecular geometry of PAH in the film. A significant portion of the polymer chains of the adsorbed PAH protrudes from the surface to form loops as shown schematically in Fig. 1, resulting in an enhanced surface density of positive charges for the binding of s-CD. It has been reported that PAH forms a coiled conformation in high ionic media as a result of shielding of electrostatic repulsion between positive charges along the polymer chain [9].

It is interesting to evaluate the binding activity of s-α-CD and s-β-CD in the multilayer films. MO was used as a model guest compound to be complexed by the s-CDs. The absorption spectra of the quartz slides coated with $(PAH–s-\alpha-CD)_{10}$ and $(PAH–s-\beta-CD)_{10}$ films are shown in Fig. 3, together with a CD-free $(PAH–PVS)_{10}$ film which contains poly(vinylsulfate) (PVS, molecular weight 242,000) in place of s-CD. The MO-adsorbed $(PAH–PVS)_{10}$ film exhibited an absorption maximum, λ_{max}, at 362 nm, which can be ascribed to aggregates of MO [10]. It is known that MO shows a blueshift upon forming aggregates, while monomeric MO exhibits λ_{max} at about 480 nm in a neutral aqueous solution [10]. MO is probably bound to PAH chains in the film by forming ion pairs because MO contains a negatively charged sulfonate residue. Even when the film was treated in lower-concentration MO solutions (10^{-5}–10^{-6} M), MO formed aggregates in the film.

On the other hand, absorption spectra of MO bound to the $(PAH–s-\alpha-CD)_{10}$ films exhibited λ_{max} at 482 nm, although a small peak was observed at 360 nm.

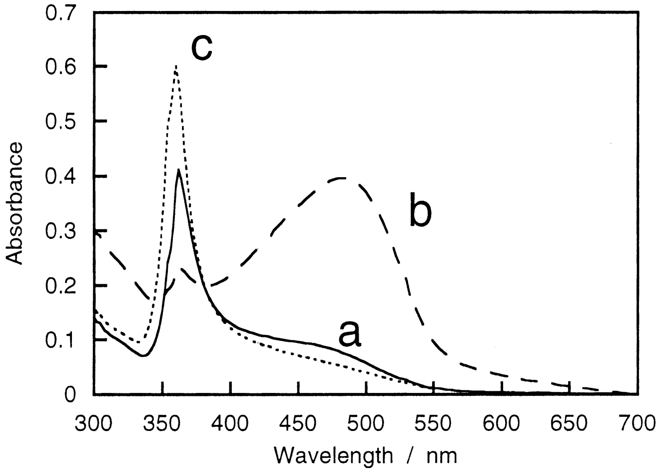

Fig. 3 UV–vis absorption spectra of methyl orange (*MO*)-bound [PAH–poly(vinylsulfate)]$_{10}$ (*a*), (PAH–s-α-CD)$_{10}$ (*b*), and (PAH–s-β-CD)$_{10}$ films (*c*)

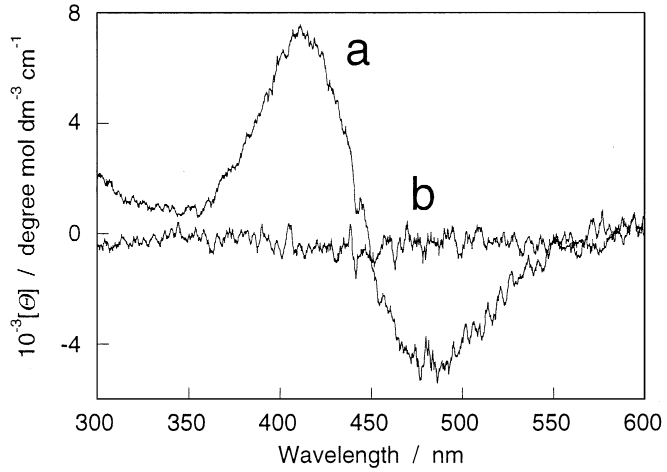

Fig. 4 Induced circular dichroism spectra of MO in the presence of s-α-CD (*a*) and s-β-CD (*b*) in solution (10 mM Tris-HCl buffer, pH 7.5). MO 4×10^{-5} M, s-α-CD or s-β-CD 1×10^{-2} M

The strong 482-nm band suggests that a large number of MO molecules are isolated as a monomer in the film, probably owing to the formation of a s-α-CD–MO inclusion complex. Thus, the (PAHs–α-CD)$_{10}$ film contains two different binding sites to MO: a s-α-CD cavity and a positive site on the PAH chain.

In contrast, the MO-adsorbed (PAH–s-β-CD)$_{10}$ film exhibited $\lambda_{\max}$ at 362 nm. In other words, the (PAH–s-β-CD)$_{10}$ film did not form an inclusion complex with MO but MO formed aggregates in the film. This is probably due to the negligibly small binding constant of MO to s-β-CD. In fact, we failed to observe any induced circular dichroism of MO in solution upon addition of s-β-CD, while s-α-CD induced a significant circular dichroism band ascribable to an inclusion complex of MO and s-α-CD (Fig. 4). The binding constant of MO to s-α-CD was determined to be about 70 M^{-1} using the induced circular dichroism spectra according to the reported procedure [11]. The positively charged environment in the PAH chains probably facilitates the binding of MO to the cavity of s-α-CD in the film.

The loading of nonaggregated MO in the (PAH–s-α-CD)$_{10}$ film was calculated to be 8.3×10^{-9} mol cm^{-2} on the basis of the absorbance at 482 nm using the molar extinction coefficient of α-CD-MO complex in solution ($\epsilon = 24{,}000$). The molar ratio of the nonaggregated MO to s-α-CD in the film is about 0.43. Judging from the MO–s-α-CD molar ratio, MO should be bound to s-α-CDs located not only on the surface of the film but at inner layers, which in turn suggests MO molecules are able to diffuse into the film smoothly. On the other hand, the content of aggregated MO in the (PAH–s-α-CD)$_{10}$ film was 1.6×10^{-9} mol cm^{-2}, which was determined using the absorbance data of aggregated MO in the (PAH–PVS)$_{10}$ film.[1] In conclusion, layered assemblies containing s-CD were constructed successfully on the surface of a quartz resonator and quartz slide by an alternate deposition of s-CD and polycation. The loading of s-CD in each layer of the films was much higher than that expected for monomolecular deposition. The s-α-CD-containing films can bind MO by forming an inclusion complex, resulting in the isolation of MO as a monomer in the film. Nearly half of s-α-CD in the film can accommodate MO. In contrast, MO formed aggregates in the s-β-CD and CD-free films. The s-α-CD-containing multilayer films may be useful for constructing functional films using various kinds of guest molecules.

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[1] The extinction coefficient of the aggregated MO was determined by extracting MO from the (PAH–PVS)$_{10}$ film into a NaOH solution (pH 12). The adsorbed MO was desorbed completely from the film by immersing the film in the NaOH solution for about 2 h

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