Switching of polymerization activity of cinnamoyl-α-cyclodextrin†

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Cinnamoyl α-cyclodextrin (α-CD) has been found to initiate polymerization of δ-valerolactone (δ-VL) to give a polymer in high yield. By the presence of the cinnamoyl group, hydrogen bond was formed between the carbonyl oxygen of δ-VL and the hydroxyl group of CD to activate the monomer, which was observed by FT-IR measurements. However, the cinnamoyl group at the C_3- and C_6-positions of α-CD did not affect the polymerization ability. Only that of the C_2-position showed high polymerization activity. The polymerization activity could be switched by the photoisomerization of the cinnamoyl group attached to the rim of α-CD. Specific monomer recognition and polymerization in the active site of the α-CD cavity was changed by the photoisomerization.

Introduction

Biological molecules change their structures depending on their external environments.[1,2] Structural control of these molecules leads to principles of molecular recognition and catalytic activities.[3–5] In the field of supramolecular chemistry, control of molecular recognition and supramolecular structures has been achieved by using external stimuli.[6–15] However, to the best of our knowledge, there is no report on the control of its catalytic function by structural changes of supramolecular architectures using external stimuli. Cyclodextrins (CDs) have been studied as enzyme models because of their selective inclusion properties with various guest molecules.[16–17] CDs promote many chemical reactions, such as hydrolysis of activated esters.[18–20] We found that CDs are useful as supramolecular synthetic reagents to give CD-tethered polyesters with threading CDs, just by mixing CDs and lactones in bulk without any co-catalyst or solvent.[21] The control of the polymerization activity of the CD was achieved by the formation of supramolecular complexes.[22] Taking the polymerization mechanism into consideration, we suppose that not only the monomer recognition by CD in an initial state but also the ester groups between the CD and the polymer chain are important for the propagation of the polymerization. Here, we have studied effects of the ester groups on the polymerization to improve and to control the polymerization activity. We used α-CD, which does not have polymerization activity for δ-valerolactone (δ-VL) by itself.

Results and discussion

Effect of esterificaton of CD on the polymerization activity

Our previous study indicated that the polymerization of lactones initiated by intact CDs showed an initial induction period, which corresponds to the formation of the inclusion complexes in bulk. After the formation of inclusion complexes, monoester-modified CD was immediately formed. When monoester-modified CD is used as an initiator, the monoester-modified CD would be expected to initiate the polymerization of lactones with high activity. To observe the difference between the polymerization activity of plain CD and that of esterified CD, we estimated the polymerization activity of esterified CD prepared from the intact CD. We chose α-CD because when intact, it does not initiate the polymerization of δ-VL at all.

The polymerization of δ-VL was carried out by heating mixture of δ-VL and α-CD (or esterified α-CD) in bulk at 100 °C ([δ-VL]/[CD] = 10). Fig. 1 shows time–yield plots for the polymerization of δ-VL initiated by α-CD and 2-*O*-*trans*-cinnamoyl-α-CD (2-*trans*-CiO-α-CD), respectively. The mixture of α-CD and δ-VL did not give any polymers. On the other hand, 2-*trans*-CiO-α-CD gave poly(δ-VL) in high yield (98% within

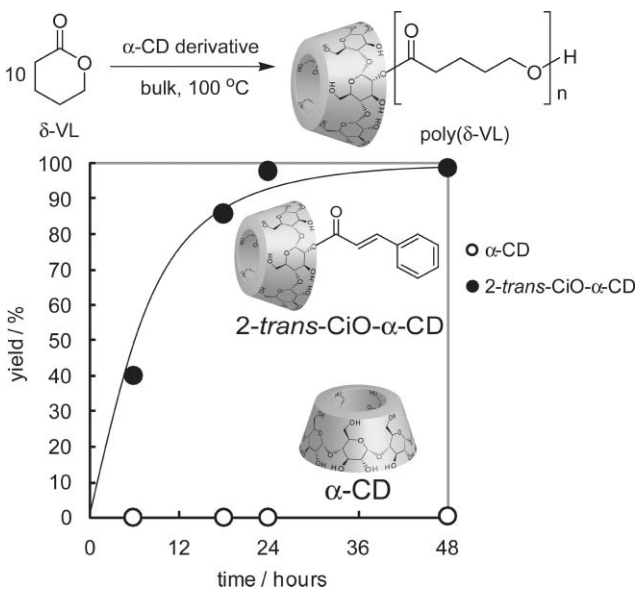

Fig. 1 Dependency of yield on time for the polymerization of δ-VL initiated by α-CD or 2-*trans*-CiO-α-CD in bulk at 100 °C. ([δ-VL]/[CD] = 10).

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48 h) under the same conditions. Other esterified CDs, such as 2-*O*-hydroxybutyrates-α-CD and 2-*O*-benzyloxypentanoyl-β-CD,[21] have also been found to initiate polymerization. These results indicate that the esterification of α-CD is important for the polymerization of δ-VL.

To validate the difference in the polymerization activity, FT-IR spectroscopy was carried out.[23] Fig. 2 shows the FT-IR spectra of δ-VL in the presence and absence of CDs. δ-VL shows a strong band due to C=O stretching at 1731.8 cm^{-1} (Fig. 2(a)). The C=O stretching band of the mixture of α-CD and δ-VL in bulk showed similar wavenumber to that of δ-VL (Fig. 2(b)), indicating that there is no intermolecular interaction between the carbonyl group of δ-VL and the hydroxyl group of α-CD. In contrast, the C=O stretching band in the mixture of 2-*trans*-CiO-α-CD and δ-VL shifted to lower wavenumber (1700.4 cm^{-1}), indicating that hydrogen bonds between the hydroxyl group of 2-*trans*-CiO-α-CD and the carbonyl group of δ-VL are formed.

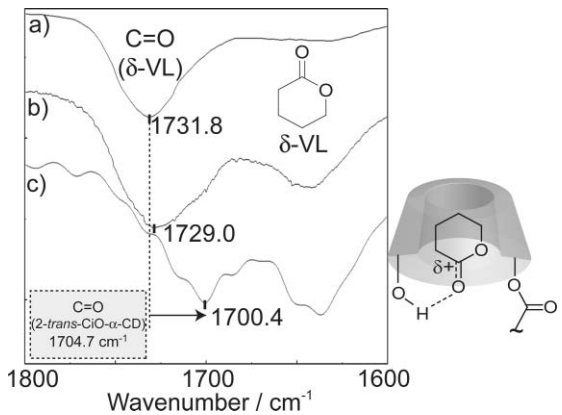


Fig. 2 FT-IR spectra of δ-VL (a), the mixture of δ-VL and α-CD (b), and the mixture of δ-VL and 2-*trans*-CiO-α-CD (c).

Okamoto[24] and Penczek[25] reported that activated heterocyclic monomers are generated by hydrogen bond formation or protonation. The formation of a hydrogen bond between CD and monomer activates the carbonyl carbon of δ-VL for nucleophilic attack. Therefore, 2-*trans*-CiO-α-CD should show polymerization activity, whereas α-CD should not initiate the polymerization.

Relationship between polymerization activity and substitution positions

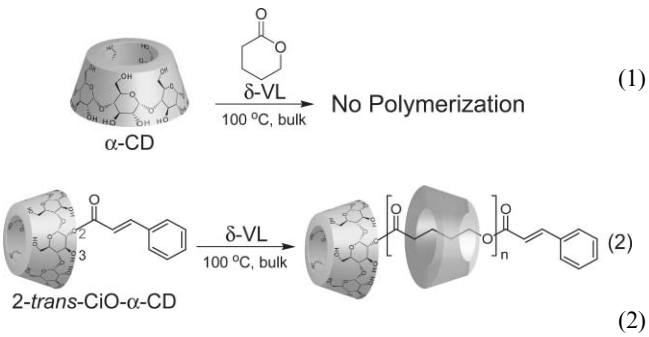
To understand the relationship between the esterification of α-CD and the enhancement of the polymerization activity, we studied the effects of the position of the cinnamoyl group on α-CD. *trans*-Cinnamic acid is able to be selectively attached to various positions on α-CD. The reaction of *m*-nitrophenyl *trans*-cinnamate and α-CD in a basic aqueous solution gave regioisomers of α-CD modified with the cinnamoyl group – 3-*trans*-CiO-α-CD and 2-*trans*-CiO-α-CD. The other isomer, 6-*trans*-CiO-α-CD, was prepared according to a literature method.[26]

δ-VL was added to these α-CD derivatives and heated to 100 °C in bulk. The results are summarized in Table 1. α-CD did not react with δ-VL after 48 h (eqn (1), entry 1 in Table 1). 2-*trans*-CiO-α-CD gave poly(δ-VL) with molecular weight (M_n, determined by GPC with polystyrene standard) of 5200 in 82% yield (eqn (2), entry 2 in Table 1) under the same conditions. After further addition of δ-VL, the product (which still has a polymerization activity) gave a longer polyester with M_n of 8100. The degree of the polymerization was more than 120, as determined by NMR spectroscopy (entry 3 in Table 1).

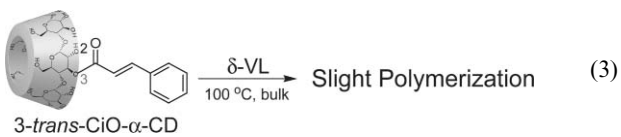
Table 1 Polymerization of δ-VL initiated by α-CD derivatives in bulk[a]

Entry	CD	Yield/%	M_n[b]	Degree of polymerization[c]
1	α-CD	0	—	0.0
2	2-*trans*-CiO-α-CD	82	5200	41.3
3[d]	Product of entry 2	58	8100	125.0
4	3-*trans*-CiO-α-CD	7	1900	3.7
5	6-*trans*-CiO-α-CD	1	1500	3.6
6	2-*trans*-CiO-α-CD ⊃CiOMe	0	0	0
7	2-*cis*-CiO-α-CD	12	2100	8.1

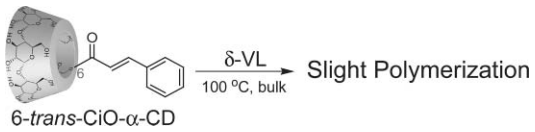
[a] [δ-VL]/[CD] = 20. The mixtures of CD and δ-VL were heated at 100 °C for 48 h. [b] The molecular weights were calibrated by GPC calculated with polystyrene standard (eluent: THF). [c] Determined by the ^{1}H NMR value of the polymer chain. [d] Before the polymerization, the polymer product of entry 2 was included into native α-CDs to form poly-*pseudo*-rotaxane.[20c]



Although 2-*trans*-CiO-α-CD showed high polymerization activity for δ-VL, 3-*trans*-CiO-α-CD and 6-*trans*-CiO-α-CD showed significantly lower polymerization activity, respectively (eqn 3 and 4, entries 4 and 5 in Table 1). These results indicate that the esterifications at C_3 and C_6 do not affect the polymerization ability. The ester group at C_2 of α-CD is thus essential for the polymerization. The secondary hydroxyl groups (at C_2 and C_3) of CD have higher basicity than those of primary ones (at C_6). Moreover, whereas 3-*trans*-CiO-α-CD has the ester group of the cinnamoyl substituent at the C_3-carbon orientating outside the CD cavity, that of 2-*trans*-CiO-α-CD locates nearby the CD cavity, which was characterized by single crystal X-ray analysis.‡



‡ The data were collected on a Rigaku RAXIS-RAPID diffractomer. A crystal, of dimensions 0.25 × 0.25 × 0.15 mm, was selected and mounted on a 0.30 mm MicroMount and immediately placed on the goniometer head in a 100.1 K N_2 gas stream. Data integration, reduction, collections for absorption and polarization effects were all performed using PROCESS-AUTO and CrystalStructure software. Space group determination, structure solution and refinement were obtained using Crystalstructure ver. 3.7 and SHELXL software. Crystal data: $C_{45}H_{66}O_{31}\cdot 12.6245H_2O$, M = 1330.36, orthorhombic, a = 15.5665(4), b = 23.5385(5), c = 33.1929(9) Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, U = 12162.3(5) Å^3, T = 100.1 K, space group $P2_12_12_1$, Z = 8, μ(Cu-Kα) = 1.54187 mm^{-1}, 99451 reflections collected, 21089 unique, (R_{int} = 0.043), R = 0.0698, wR^2 = 0.2154.



(4)

The product obtained from the mixture of 2-*trans*-CiO-α-CD and δ-VL was characterized by ^{1}H NMR and MALDI-TOF mass spectroscopy (Figs. S1 and S2†). The product obtained from the mixture of 2-*trans*-CiO-α-CD and δ-VL has a single poly(δ-VL) chain propagated from the ester bond at the C_2-position of 2-*trans*-CiO-α-CD.

The polymerization ability of 2-*trans*-CiO-α-CD is improved by the following. (i) The cinnamoyl group of 2-*trans*-CiO-α-CD is activated by the formation of hydrogen bonds between the carbonyl oxygen of the *trans*-cinnamoyl group and the secondary hydroxyl groups of CD. (ii) The hydroxyl group at the end of monomer might be easily attached to the carbonyl carbon of the cinnamoyl group at C_2 and thus propagate from C_2 because the ester group of the cinnamoyl group is located adjacent to the included monomer.

We investigated the inhibition of the initiation reaction of δ-VL by using a competitive guest. Methyl *trans*-cinnamate (CiOMe; association constant $K_a = 1200$ M^{-1} for the α-CD cavity[27]) was used as a competitive guest for δ-VL ($K_a = 10$ M^{-1} for α-CD). The inclusion complex of 2-*trans*-CiO-α-CD with CiOMe (2-*trans*-CiO-α-CD⊃CiOMe) showed no polymerization activity (entry 6 in Table 1). It should be considered that δ-VL was not included in the cavity of 2-*trans*-CiO-α-CD because CiOMe is strongly included in the cavity. These observations suggest that the cavity of 2-*trans*-CiO-α-CD is the active site for the polymerization of δ-VL.

Switch of polymerization activity

We supposed that control of the molecular recognition might lead to control of the initiation reaction – inhibition of the monomer binding in the α-CD cavity would lead to the inhibition of the polymerization. We investigated the control of the polymerization by using 2-*trans*-CiO-α-CD. The initiation step would be prevented by the photoisomerized cinnamoyl group if the photoisomerized substituent acted as a 'ledge', restricting monomer inclusion at the rim of the α-CD cavity. In aqueous solution, 2-*trans*-CiO-α-CD was irradiated by UV light ($\lambda = 280$ nm) to give 2-*cis*-CiO-α-CD (Fig. 3), which was purified by preparative reverse-phase HPLC. A mixture of 2-*cis*-CiO-α-CD and δ-VL gave only 12% of poly(δ-VL) with lower M_n under the same conditions (entry 7 in Table 1), indicating that the polymerization activity of 2-CiO-α-CD was restricted by using the photoisomer of the cinnamoyl α-CD. Thus, the *cis*-cinnamoyl group seems to inhibit the binding of monomer in the 2-CiO-α-CD cavity.

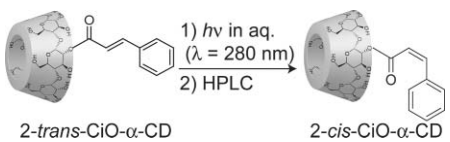


Fig. 3 Schematic illustration of photoisomerization of 2-CiO-α-CD.

The FT-IR spectra of the mixture of δ-VL and 2-*trans*-CiO-α-CD showed a large shift of the band for the carbonyl group of δ-VL to shorter wavenumber (1700.4 cm^{-1}) (Fig. 4(c)), indicating that the inclusion and the activation of the monomer took place in the CD cavity *via* hydrogen bond formation. On the other hand, the mixture of δ-VL and 2-*cis*-CiO-α-CD did not show such a shift (Fig. 4(e)), suggesting that 2-*cis*-CiO-α-CD and δ-VL did not show this interaction. These results suggest that δ-VL was included only in the cavity of 2-*trans*-CiO-α-CD and that the CD cavity functions as the active site for the polymerization. The aromatic ring of the cinnamoyl group of 2-*cis*-CiO-α-CD significantly inhibits the formation of the inclusion complex.

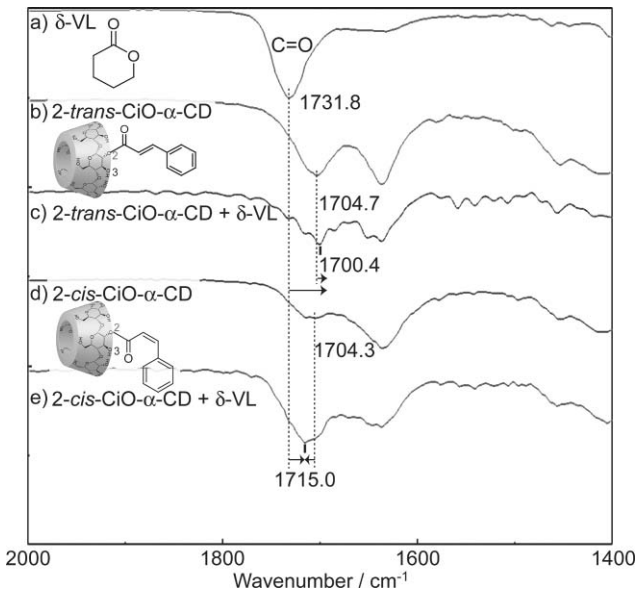
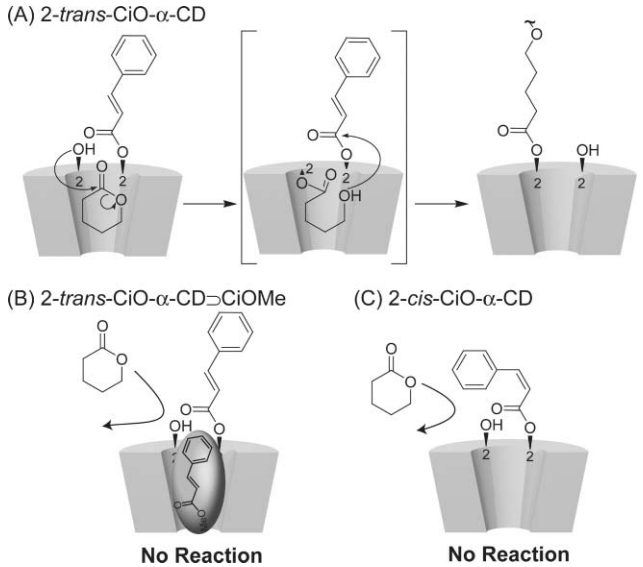


Fig. 4 FT-IR spectra of δ-VL (a), 2-*trans*-CiO-α-CD (b), a mixture of δ-VL and 2-*trans*-CiO-α-CD (c), 2-*cis*-CiO-α-CDs (d), and a mixture of δ-VL and 2-*cis*-CiO-α-CD (e). (KBr-disc method).

Scheme 1 shows a proposed propagation mechanism for the polymerization of δ-VL by 2-CiO-α-CDs. First, 2-*trans*-CiO-α-CD includes δ-VL in its cavity, then the hydroxyl group of CD attacks the carbonyl carbon of δ-VL to open the ring. The generated hydroxyl group of the monomer immediately attacks the ester bond of 2-*trans*-CiO-α-CD to insert δ-VL into the ester bond between the cinnamoyl group and α-CD, so as to give a single poly(δ-VL) chain attached to α-CD at the C_2-position. Another new δ-VL is accepted by the cavity to continue the propagation step to produce poly(δ-VL) chain from the CD moiety (Scheme 1(A)). However, it should be noted that the 2-*trans*-CiO-α-CD⊃CiOMe inclusion complex showed no polymerization activity due to the inhibition of monomer recognition (Scheme 1(B)). After the photoisomerization, 2-*cis*-CiO-α-CD did not initiate the polymerization. The substituent of 2-*cis*-CiO-α-CD might limit monomer inclusion, acting as a 'ledge' at the rim of active site of the CD cavity. The approach of δ-VL is inhibited by the presence of bulky *cis*-cinnamoyl group (Scheme 1(C)).

Conclusions

In conclusion, α-CD modified with ester groups at C_2-position has been found to show polymerization activity for δ-VL, whereas free α-CD did not initiate the polymerization. The polymerization takes place in the CD cavity. We have succeeded in switching the



Scheme 1 Proposed mechanisms of the propagation step by 2-*trans*-CiO-α-CD (A) and the inhibition of the propagation by 2-*trans*-CiO-α-CD⊃CiOMe (B) and 2-*cis*-CiO-α-CD (C).

initiation activity of the polymerization by the photoisomerization of the cinnamoyl group at the C_2-position. This polymerization system showed specific substrate recognition, releasing the products from the active site, and is similar to those of enzymes having highly sophisticated functions. Application of this system to polymerization of other molecules are now under investigation.

Experimental section

General procedures

All manipulations were carried out using standard Schlenk techniques under an argon atmosphere. Tetrahydrofuran (THF) was dried and deoxygenated by distillation over sodium benzophenone ketyl under an argon atmosphere. *N*,*N*-Dimethylformamide (DMF) was dried and deoxygenated by distilling from BaO under reduced pressure. α-Cyclodextrin (α-CD) was obtained from Junsei Chemical Co., Ltd. δ-Valerolactone (δ-VL) was obtained from Nacalai Tesque. Cyclodextrins were used after drying under vacuum at 80 °C. Lactones were distilled over CaH_2 under an argon atmosphere and dried over molecular sieves (4 Å). The photoisomerization was performed using an Asahi Spectra Compact Xenon Light Source MAX-301 (300 W) with $\lambda = 280$ nm band pass filter (±10 nm).

Measurements

^{1}H (500 and 600 MHz) and ^{13}C (125 and 150 MHz) NMR spectra in DMSO-d_6 were measured on JEOL JNM-LA500 and VARIAN INOVA 600 spectrometers. Assignments of ^{1}H and ^{13}C NMR peaks for some complexes were supported by 2D ^{1}H–^{1}H NOESY, 2D ^{1}H–^{1}H COSY, 2D TOCSY, 2D HMQC and 2D HMBC spectra. MALDI-TOF mass spectra measurements were performed on a Shimadzu/KRATOS AXIMA-CFR spectrometer. FT-IR spectra were measured on a JASCO FT/IR-410 spectrometer with KBr discs. Gel-permeation chromatography (GPC) was performed using a TOSOH GPC system with a TOSOH G3000HXL and G2000HXL column (eluent: THF, detector: refractive index and UV absorbance ($\lambda = 256$ nm)). Isothermal titration calorimetry (ITC) was performed using a MicroCal VP-ITC MacroCalorimeter to determine the association constant of CDs.

Preparation of *trans*-cinnamoyl-α-CDs (*trans*-CiO-α-CDs)

6-*trans*-CiO-α-CD was prepared by a previously reported method.[22] 2- and 3-*trans*-CiO-α-CD were prepared by the following method.

(i) Preparation of *m*-nitrophenyl cinnamate (*m*-NPC). *trans*-Cinnamic acid (6.1 g, 41 mmol), *m*-nitorphenol (5.8 g, 41 mmol), and *N*,*N*′-dicyclohexyl-carbodiimide (8.5 g, 41 mmol) were dissolved in THF (37 mL), and stirred for 24 h at room temperature. After removal of the undissolved residue by filtration, the filtrate was poured into 800 mL water. The resulted precipitate was washed with a saturated aqueous solution of sodium hydrogen carbonate once and recrystallized twice from *n*-butanol. ^{1}H NMR (DMSO-d_6, 20 °C, 500 MHz): δ 6.90 (d, $J = 16.1$ Hz, 1H, -C*H*=CH-Ph), 7.44–7.50 (m, 3H, -CH=CH-*3*,*4*,*5*-*Ph*), 7.71–7.78 (m, 3H, *6*-*Ph*-NO_2), 7.79–7.85 (m, 2H, -CH=CH-*2*,*6*-*Ph*), 7.91 (d, $J = 16.1$ Hz, 1H, -CH=C*H*-Ph). Elemental Anal. Calcd for $C_{15}H_{11}NO_4$: C, 66.91; H, 4.12; N, 5.20. Found: C, 66.79; H, 3.96; N,5.21.

(ii) Preparation of cinnamoyl-attached α-cyclodextrins (CiO-α-CDs). α-CD (1.5 g, 1.6 mmol) was dissolved in 300 mL of 0.40 mM sodium carbonate solution containing 180 mL of acetonitrile. *m*-NPC (0.60 g, 2.2 mmol) dissolved in 30 mL of acetonitrile was gradually added to the α-CD solution with stirring. The pH of the reaction medium was adjusted to 8–9 by the addition of 0.10 M NaOH solution at room temperature. After 2 h, the reaction solution was adjusted to pH 3 with 1.0 M HCl solution. The reaction mixture was lyophilized to give colorless powder. The crude powder was washed with water (200 mL) to get rid of the insoluble compounds. The contaminants in the filtrate were removed by the extration with 600 mL of ether. The aqueous layer was lyophilized to give 2-*trans*-CiO-α-CD and 3-*trans*-CiO-α-CD. Reversed-phase preparative HPLC (colomn: SunFire C_{18}-SemiPrep, solvent: water–acetonitrile) was performed to separate these isomers. The lyophilized powder was dissolved in 50 mL of distilled water and an aliquot of the solution (5.0 mL) was injected onto HPLC system. **2-*trans*-CiO-α-CD:** ^{1}H NMR (D_2O, 20 °C, 600 MHz): δ 7.88 (d, $J = 16.0$ Hz, 1H, -CH=C*H*-Ph), 7.86 (d, $J = 6.6$ Hz, 2H, -CH=CH-2,6-*Ph*), 7.65 (t, $J = 7.5$ Hz, 2H, -CH=CH-3,5-*Ph*), 7.51 (t, $J = 7.4$ Hz, 1H, -CH=CH-*4*-*Ph*), $C^B(2)H$, 6.82 (d, $J = 16.0$ Hz, 1H, -C*H*=CH-Ph), 5.29 ($C^A(1)H$), 5.07 ($C^F(1)H$), 5.01 ($C^E(1)H$), 5.00 ($C^B(1)H$), 4.98 ($C^C(1)H$), 4.91 ($C^D(1)H$), 4.67 ($C^A(2)H$), 4.67 ($C^A(3)H$), 4.11 ($C^E(3)H$), 4.03 ($C^B(3)H$), 3.93 ($C^A(3)H$), 3.89 ($C^E(4)H$), 3.47–3.98 ($C^{A\text{-}F}(5)H$, $C^{A\text{-}F}(6)H$, $C^B(4)H$, $C^C(3\text{–}4)H$), 3.84 ($C^C(3)H$, $C^F(3)H$), 3.62 ($C^C(4)H$, $C^E(2)H$), 3.60 ($C^F(2)H$), 3.53 ($C^F(4)H$, $C^C(2)H$), 3.52 ($C^A(4)H$, 3.51 ($C^D(2)H$). ^{13}C NMR (D_2O 20 °C, 150 MHz): δ 168.9 (–O-*C*=O), 146.6 (–CH=*C*H-Ph), 134.4 (–CH=CH-1-*Ph*), 130.7 (–CH=CH-4-*Ph*), 129.5 (–CH=CH-3,5-*Ph*), 128.8 (–CH=CH-2,6-*Ph*), 117.4 (–*C*H=CH-Ph), 99.0, 82.1, 73.6, 71.5, 70.5, 60.5, (C^A(1–6) of CD moiety), 101.9, 101.8, 101.7, 81.7, 81.4, 73.9, 73.4, 73.3, 73.1, 72.6, 72.4, 72.3, 72.2,

72.1, 71.9, 71.8, 71.7, 60.9, 60.7, 60.3 (C^{B-F}(1–6) of CD moiety). MALDI-TOF MS; m/z = 1126.1 ($[C_{45}H_{66}O_{31} + Na]^+$ = 1125.4), 1142.2 ($[C_{45}H_{66}O_{31} + K]^+$ = 1141.3). Elemental Anal. Calcd for $C_{45}H_{66}O_{31}(H_2O)_6$: C, 44.63; H, 6.49. Found: C, 44.81; H, 6.28. **3-*trans*-CiO-α-CD:** ^{1}H NMR (D_2O, 20 °C, 600 MHz): δ 8.06 (d, J = 16.0 Hz, 1H, -CH=C*H*-Ph), 7.88 (d, J = 16.0 Hz, 2H, -CH=CH-*2*, *6-Ph*), 7.59 (t, J = 7.4 Hz, 2H, -CH=CH-*3*, *5-Ph*), 7.53 (t, J = 7.4 Hz, 1H, -CH=CH-*4-Ph*), 6.70 (d, J = 16.0 Hz, 1H, -C*H*=CH-Ph), 5.66 (C^A(3)*H*), 5.13 (C^A(1)*H*), 5.01 (C^F(1)*H*), 5.08 (C^E(1)*H*), 5.06 (C^D(1)*H*), 4.94 (C^B(1)*H*), 4.91 (C^C(1)*H*), 4.14 (C^D(3)*H*), 4.01 (C^A(5)*H*), 3.37–4.05 ($C^{B,E,F}$(6)*H*, C^C(3–6)*H*), 3.91 (C^A(4)*H*, C^F(4)*H*), 3.89 (C^E(5)*H*), 3.87 (C^A(2)*H*), 3.85 (C^A(6)*H*), 3.84 (C^F(3)*H*), 3.83 (C^E(3)*H*), 3.82 (C^D(5)*H*), 3.66 (C^D(2)*H*), 3.65 (C^D(6)*H*), 3.64 (C^B(5)*H*, C^F(5)*H*), 3.62 (C^D(4)*H*), 3.60 (C^E(2)*H*), 3.58 (C^F(2)*H*), 3.53 (C^E(4)*H*, C^C(2)*H*), 3.51 (C^B(3)*H*), 3.41 (C^B(2)*H*, C^B(4)*H*). ^{13}C NMR (D_2O 20 °C, 150 MHz): δ 170.0 (–O-*C*=O), 147.0 (–CH=*C*H-Ph), 135.1 (–CH=CH-*1-Ph*), 131.1 (–CH=CH-*4-Ph*), 129.7 (–CH=CH-*3*,*5-Ph*), 129.3 (–CH=CH-*2*,*6-Ph*), 118.2 (–*C*H=CH-Ph), 101.8, 81.6, 79.7, 75.6, 73.7, 71.4, (C^A(1–6) of CD moiety), 102.3, 102.2, 102.1, 102.0, 82.1, 82.0, 81.9, 81.8, 74.3, 73.8, 73.5, 73.3, 72.9, 72.7, 72.6, 72.5, 72.3, 72.2, 71.5, 61.2, 61.1, 61.0, 60.8 (C^{B-F}(1–6) of CD moiety). MALDI-TOF MS; m/z = 1125.4 ($[C_{45}H_{66}O_{31} + Na]^+$ = 1125.4), 1142.3 ($[C_{45}H_{66}O_{31} + K]^+$ = 1141.3). Elemental Anal. Calcd for Calcd for $C_{45}H_{66}O_{31}(H_2O)_5$: C, 45.30; H,6.42. Found: C, 45.02; H, 6.35.

Polymerization of lactones initiated by CDs in bulk

All the procedures of the polymerization of lactones by CDs were carried out by the following method. 2-*trans*-CiO-α-CD (9.1 μmol, 10.0 mg) was dried *in vacuo* at 80 °C for 24 h. Then, δ-valerolactone (180 mmol, 18 mg) was added to 2-*trans*-CiO-α-CD under an argon atmosphere. The reaction tube was sealed under an argon atmosphere, and kept at 100 °C with stirring. After the prescribed reaction time, the polymerization was terminated by adding a large amount of dry DMF (1.0 mL). The resulting powder was dissolved in DMF. The resultant polymer solution was added to THF (10.0 mL) to precipitate free CD. The filtrate was evaporated *in vacuo* to obtain polyester (Yield: 82%). ^{1}H NMR (DMSO-d_6, 30 °C, 500 MHz): δ 7.57 (m, 1H, *p*-cinnamate), 7.53 (d, J = 8.2 Hz, 1H, α-cinnamate), 7.39 (d, J = 8.2 Hz, 2H, *o*-cinnamate), 7.23 (m, 2H, *m*-cinnamate), 6.54 (m, 1H, β-cinnamate), 5.49 (br, 11H, $O_{2,3}H$), 4.79 (br, 5H, C_1H), 4.46 (br, 6H, O_6H), 4.36 (br, 1H, C_1'H), 4.00 (br, 4H, δ-polymer), 3.76 (br, 12H, C_6H), 3.63 (br, 12H, $C_{35}H$), 3.37 (br, 12H, $C_{4,2}H$), 2.27 (br, 4H, α-polymer), 1.55 (br, 8H, γ- and β-polymer). To show detailed structure of terminal cinnamoyl unit, the NMR sample was prepared by HPLC to obtain lower molecular weight moiety. IR (KBr): 3396, 2932, 1704, 1643 cm^{-1}.

Preparation of 2-*cis*-CiO-α-CD (photoisomerization)

2-*trans*-CiO-α-CD (50 mg) was dissolved in water (20 mL). The solution was irradiated by Asahi Spectra Compact Xenon Light Source MAX-301 (wavelength: $\lambda = 280 \pm 10$ nm) in ice bath for 24 h. The solution was lyophilized to obtain white powder, then 2-*cis*-CiO-α-CD was isolated with reverse-phase HPLC. (Yield: 32 mg, 64%) ^{1}H NMR (DMSO, 30 °C, 500 MHz): δ 7.65 (d, 2H, -CH=CH-*2*,*6-Ph*), 7.34–7.36 (t, 2H, -CH=CH-*3*,*4*,*5-Ph*), 6.97 (d, J = 13.0 Hz, 1H, -CH=C*H*-Ph), 6.11 (d, J = 13.0 Hz, 1H, -C*H*=CH-Ph), 5.35–5.69 (m, 11H, O(2,3)*H*), 5.02 (C(1″)*H*), 4.84 (C(1′)*H*), 4.79 (*m*, 4H, C(1)*H*), 4.38–4.58 (m, 6H, O(6)*H*), 4.06 (C(2′)*H*), 3.52–3.88 (*m*, 22H, C(3)*H*, C(5)*H* and C(6)*H*), 3.16 (C(6′)*H*), 3.20–3.49 (m, C(2)*H* and C(4)*H* overlapped with HOD). MALDI-TOF MS; m/z = 1125.7 ($[C_{45}H_{66}O_{31} + Na]^+$ = 1125.4). Elemental Anal. Calcd for $C_{45}H_{66}O_{31}(H_2O)_7$: C, 43.97; H, 6.56. Found: C, 43.68; H, 6.26.

Preparation of 2-*trans*-CiO-α-CD⊃CiOMe inclusion complex

2-*trans*-CiO-α-CD (22 mg, 20 μmol) was dissolved in water (2 mL), and 3.2 mg (20 μmol) of methyl cinnamate (CiOMe) was added to the solution. After stirring 10 min, the solution was lyophilized and dried at 50 °C to remove excess amount of CiOMe and to obtain 1 : 1 inclusion complex of 2-*trans*-CiO-α-CD⊃CiOMe. (Yield 22 mg, 87%). ^{1}H NMR (DMSO-d_6, 30 °C, 500 MHz): δ 7.72–7.65 (m, 6H, -CH=CH-2,6-*Ph* (2-*trans*-CiO-α-CD and CiOMe)), 7.41–7.44 (m, 6H, -CH=CH-3,4,5-*Ph* (2-*trans*-CiO-α-CD and CiOMe)), 6.69 (d, J = 16.0 Hz, 1H, -C*H*=CH-Ph of 2-*trans*-CiO-α-CD), 6.63 (d, J = 16.0 Hz, 1H, -C*H*=CH-Ph of CiOMe), 5.33–5.72 (m, 11H, O(2,3)*H*), 5.03 (C(1″)*H*), 4.84 (C(1′)*H*), 4.79 (*m*, 4H, C(1)*H*), 4.34–4.60 (m, 6H, O(6)*H*), 4.06 (C(2′)*H*), 3.51–3.89 (*m*, 22H, C(3)*H*, C(5)*H* and C(6)*H*), 3.21–3.51 (m, C(2)*H* and C(4)*H* overlapped with HOD), 3.17 (C(6′)*H*). Elemental Anal. Calcd. for $C_{55}H_{76}O_{33}(H_2O)_{11}$: C, 45.14; H, 6.75. Found: C, 44.79; H, 6.38.

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