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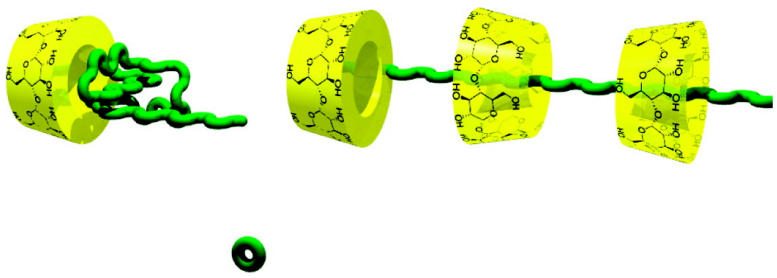

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An Artificial Molecular Chaperone: Poly-*pseudo*-rotaxane with an Extensible Axle

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Abstract: Poly-*pseudo*-rotaxanes CDs⊃**1** (CDs; cyclodextrins, **1**; poly(δ-valerolactone) having single β-CD at the end of the polymer chain) initiate polymerization of δ-valerolactone (δ-VL) in the solid state when CDs (α-CD, β-CD, and 2,6-di-*O*-methyl-β-CD) are threaded onto the polymer chain. **1** without threaded CDs did not show any polymerization ability for δ-VL. An adamantane molecule (Ad) inhibited the polymerization ability of CDs⊃**1** for δ-VL, indicating that β-CD at the end of CDs⊃**1** could not bind δ-VL because the β-CD cavity was occupied by Ad. It should be noted that the insertion reaction and the polymerization took place inside the β-CD cavity at the end of CDs⊃**1** and that the formation of poly-*pseudo*-rotaxane is necessary for the initiation of δ-VL. The structures of β-CD⊃**1** and **1** were characterized by powder X-ray diffraction measurements and solid-state NMR spectroscopies. The polymer chain of β-CD⊃**1** was found to elongate in the solid state, whereas the polymer chain of **1** formed a random coil conformation. **1** was deactivated for the polymerization by blocking the active cavity of β-CD with the polymer chain. CDs threaded onto **1** are immune to the initiation of δ-VL directly but have an essential role to fold the polymer chain in a proper way as an artificial chaperone.

Introduction

Recently, artificial systems inspired by living systems have attracted much attention from both chemists and biologists. In biological system, there are some cyclic architectures, such as DNA polymerase, RNA polymerase, and λ-exonuclease, that encircle linear polymers to give rotaxane structures.[1−3] Chaperone proteins help to keep a protein in a proper conformation by complex formation with folded peptides.[4−9] Cyclodextrins (CDs), which also have a cylindrical structure, form inclusion complexes with various substrates and have fascinated many researchers as an enzyme model.[10−18] We observed the formation of inclusion complexes of some polymers with CDs[19−23] and reported the supramolecular polymer complexes, such as rotaxanes[24−26] and nanotubes.[27] Nolte and co-workers reported a *pseudo*-rotaxane catalyst for epoxidation of polybutadiene by a toroidal metalloporphyrin.[28] However, no rotaxanes, in which an axis molecule possesses the ability to grow up, have been reported. We found that CDs selectively include some lactones and initiate the polymerizations to give polyesters having a single CD molecule at the end of the polyester only by mixing CD and lactones.[29] Here, we have supposed that the polyesters having a CD would still have the ability to polymerize lactones. In this paper, we show the construction of a novel poly-*pseudo*-rotaxane with a growing polyester having a CD. Although the axis molecule itself did not show polymerization activity for

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Table 1. Polymerizations of δ-VL by **1** or Poly-*pseudo*-rotaxane (β-CD⊃**1**) in Bulk at 100 °C[a]

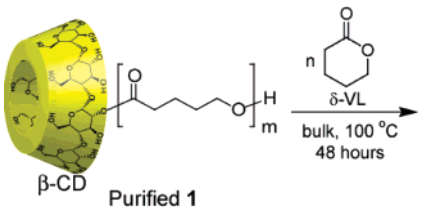
entry	initiator	no. of β-CD/ no. of δ-VL units[b]	[δ-VL]/ [CDs⊃**1**]	conv/ %	M_n[c]	M_w/M_n[c]
1	**1**	0/20	20	0	2 300	1.9
2	β-CD⊃**1**	4/20	20	32	3 600	1.6
3	β-CD⊃**1**	14/20	20	76	5 800	2.4
4	β-CD⊃**1**	23/46	100	38	11 100	1.7

[a] **1** or β-CD⊃**1** was heated with δ-VL in bulk at 100 °C for 48 h. [b] The numbers of β-CDs and δ-VL units in the initiators were determined by the integral values from ^{1}H NMR spectroscopy. [c] The M_n and M_w/M_n were determined by gel-permeation chromatography and calibrated by polystyrene standards. M_n values of **1** were 2300 (entries 1 and 2) or 7400 (entry 3) before the postpolymerization.

lactone, it showed activity with the formation of poly-*pseudo*-rotaxane. We have revealed that not only CD at the end of polymer but also the poly-*pseudo*-rotaxane structure plays an important role in the polymerization of lactone.

Results and Discussion

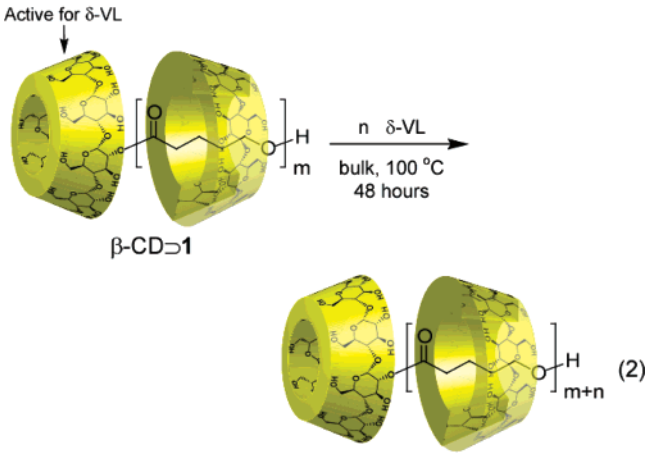
Preparation of Polyester-Tethered CD and Its Polymerization Activity for Lactone. An axis molecule, β-CD-tethered poly(δ-valerolactone) (**1**), was prepared by heating at heterogeneous mixture of β-CD and δ-valerolactone (δ-VL) at 100 °C in bulk.[29] The crude **1**, containing nonreacted β-CD, was dissolved in *N*,*N*-dimethylformamide (DMF), and the solution was added to tetrahydrofuran (THF) to remove nonreacted β-CD as precipitate. The filtrate containing excess δ-VL was evaporated in vacuo to give purified **1**. We thought that the β-CD at the end of **1** would be able to include new lactones to initiate the polymerization of the lactones and that the lactones would be inserted into the CD−polyester linkage to give a longer polyester.[29] However, heating **1** with δ-VL did not change the molecular weight (M_n) of **1** at all (eq 1; entry 1 in Table 1), indicating that **1** was inactive for polymerization of lactone.



No reaction (1)

We supposed that the topological structure of **1** with intact CDs is important to initiate the polymerization again to give longer polymers. Therefore, to obtain poly-*pseudo*-rotaxane with β-CD (β-CD⊃**1**), purified **1** was added to the β-CD-saturated aqueous solution. β-CD⊃**1** showed polymerization activity for δ-VL (eq 2). The M_n of **1** increased from 2300 to 5800 when 20 equiv of δ-VL was added to β-CD⊃**1** (entry 3 in Table 1). The post-polymerization of **1** with M_n of 7400 gave **1** with M_n of 11 100 (entry 4 in Table 1). After the polymerization of δ-VL with β-CD⊃**1**, no lower-molecular-weight polymer was observed in the gel permeation chromatography (GPC) diagrams (see Supporting Information, Figure S1). The MALDI-TOF mass spectrum did not show the spectra of poly(δ-VL) without β-CD. These results indicate that only an axis molecule of β-CD⊃**1** is elongated by the polymerization (Supporting Information, Figure S2).

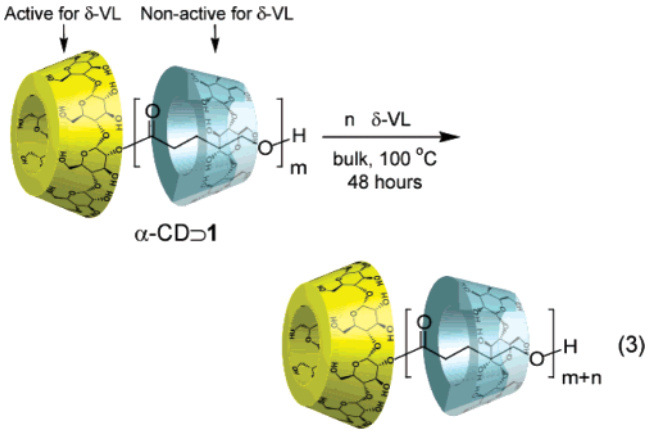
To investigate the relationship between the polymerization activity and the threading level of β-CD for the polymer chain,



(2)

the polymerization of δ-VL was carried out by using two kinds of β-CD⊃**1** with different threading levels of β-CD. β-CD⊃**1** with higher threading level (entry 3 in Table 1) showed higher polymerization ability than β-CD⊃**1** with lower threading level (entry 2). These results indicate that the polymerization activity depended on the number of CDs threaded onto the polymer chain and that the formation of the poly-*pseudo*-rotaxane is important to keep their active state.

Investigation of the Active Site of CDs⊃1. To investigate the behavior of the additional CDs threaded onto the purified **1**, α-CD and 2,6-di-*O*-methyl-β-CD (DM-β-CD) were employed as threading rings of the poly-*pseudo*-rotaxanes (CDs⊃**1**) because α-CD and DM-β-CD did not show any polymerization activity for δ-VL.[29] α-CD⊃**1** and DM-β-CD⊃**1** were prepared by mixing **1** and a saturated aqueous solution of the corresponding CD. Although α-CD or DM-β-CD threaded onto **1** cannot initiate the polymerization of δ-VL, the M_n values of α-CD⊃**1** and DM-β-CD⊃**1** were increased upon heating with δ-VL (eq 3; entries 1 and 2 in Table 2). These results indicate that only β-CD at the end of **1** can initiate polymerization of the poly-*pseudo*-rotaxane CD⊃**1**.



(3)

Moreover, we investigated the inhibition of polymerization for δ-VL by a competitive guest. Adamantane (Ad) was used as a competitive guest which is strongly included in the cavity of β-CD.[30] β-CD⊃**1**⊃Ad (β-CD⊃**1** with Ad included in the β-CD cavity at the end of **1**) was prepared by mixing β-CD⊃**1** and Ad in water ([**1**]:[Ad] = 1:1 in β-CD⊃**1**⊃Ad). β-CD⊃**1**⊃Ad

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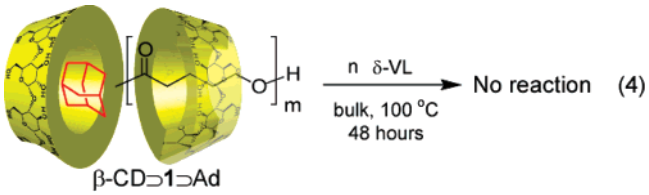
Table 2. Polymerizations of δ-VL by Poly-*pseudo*-rotaxanes (CDs⊃**1**) in Bulk at 100 °C[a]

entry	initiator	no. of CDs/ no. of δ-VL units[b]	[δ-VL]/ [CDs⊃**1**]	conv/ %	M_n[c]	M_w/M_n[c]
1	α-CD⊃**1**	14/20	20	61	6,000	2.2
2	DM-β-CD⊃**1**	11/20	20	62	5,200	2.7
3	β-CD⊃**1**⊃Ad	13/20	20	0	2,400	1.9
4	α-CD⊃**1**⊃Ad	11/20	20	0	2,300	1.7

[a] CDs⊃**1** were heated with δ-VL in bulk at 100 °C for 48 h. [b] The numbers of CDs and δ-VL units in the initiators were determined by the integral values from ^{1}H NMR spectroscopy. [c] The M_n and M_w/M_n values were determined by gel permeation chromatography and calibrated by polystyrene standards. M_n of **1** was 2300 before the postpolymerization.

showed no polymerization activity for δ-VL (eq 4; entry 3 in Table 2). We also confirmed that α-CD⊃**1**⊃Ad showed no polymerization activity (entry 4 in Table 2). It should be considered that δ-VL was not included in the β-CD at the end of CDs⊃**1**⊃Ad. These observations suggest that the β-CD at the end of **1** is the active site for the polymerization of δ-VL and that the unmodified CDs threaded onto **1** have no polymerization activity. The unmodified CDs threaded onto **1** cannot include δ-VL because they have already included the polymer chain of **1** in their cavities. These threading CDs are supposed to play a supplementary role to control the structure of **1** in the polymerization.



Propagation Step Observed by Solid-State NMR. The polymerization behavior in bulk was studied by the ^{13}C 1pda/MAS NMR (single pulse with ^{1}H decoupling/magic angle spinning NMR). The 1pda/MAS NMR spectra support the polymerization behavior of δ-VL at 100 °C in solid state because the 1pda/MAS NMR method enhances the peak intensity for mobile regions in the sample with the nuclear Overhauser effect (NOE) for the ^{13}C by saturating the proton resonances. Figure 1a shows the time course of ^{13}C 1pda/MAS NMR spectra for the mixture of β-CD⊃**1** and δ-VL at 100 °C. Although the signals of δ-VL (a−d) were observed in the early stage, the peak intensities of δ-VL decreased with time, and those of poly(δ-VL) (A−D) appeared. The conversions of δ-VL to poly(δ-VL) were determined by the integral values of δ-VL and poly(δ-VL). Figure 1b shows the time−conversion curves for the polymerizations of δ-VL using β-CD⊃**1** and **1**. It should be noted that the conversion of poly(δ-VL) increased with time in the mixture of β-CD⊃**1** and δ-VL, but the mixture of the purified **1** and δ-VL did not show an increase in the conversion with time. These results are consistent with the polymerization activities of β-CD⊃**1** and **1** in Table 1.

Dynamic Behavior of a Polymer Chain Observed by Spin−Lattice Relaxation Time Measurements. Spin−lattice relaxation times (T_1) of **1** and β-CD⊃**1** were measured with the solid-state NMR technique.[31] Polymers in the solid state are well known to show two kinds of T_1, which are derived

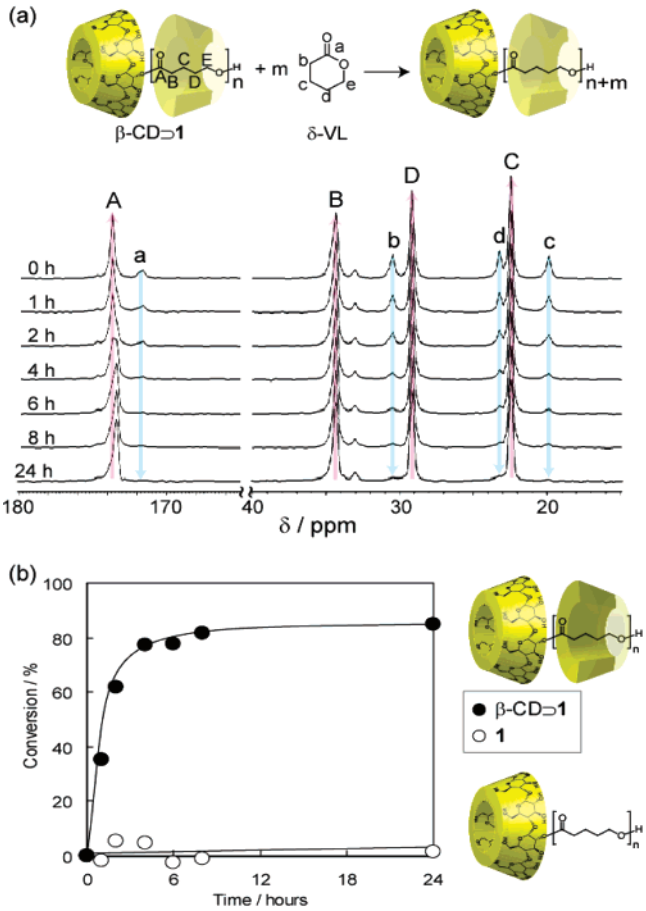
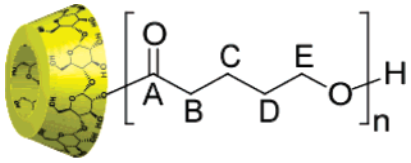


Figure 1. Time course of ^{13}C 1pda/MAS NMR spectra of a mixture of β-CD⊃**1** and δ-VL at 100 °C (a), and the time−conversion curve of the polymerization of δ-VL with β-CD⊃**1** and with **1** (b).

Table 3. Spin−Lattice Relaxation Time (T_1, s) Values for **1** and β-CD⊃**1** in Bulk



	C_A	C_B	C_C	C_D	C_E
1	262.7	78.3	82.7	77.3	90.8
	20.3	0.65	0.67	0.56	0.67
β-CD⊃**1**	4.5	0.28	0.28	0.28	0.52

from the crystalline region and the amorphous region. T_1 of the amorphous region is shorter than that of the crystalline region.[32] We focused on the shorter T_1 of polymer chains to find out the dynamic behavior of polymer chains in the amorphous region (Table 3).[33,34] T_1 values of β-CD⊃**1** were shorter than those of **1**, indicating that the polymer chain in β-CD⊃**1** has a higher mobility than that in **1**. The increase in the mobility of the polymer chain of β-CD⊃**1** is due to the fact that the polymer chain is isolated from the neighboring polymer chain to be given some space by β-CD. These results indicate that the polymer

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(32) Kaji, H.; Horii, F. *Macromolecules* **1997**, *30*, 5791−5798.
(33) Porbeni, F. E.; Shin, I. D.; Shuai, X.; Wang, W.; White, J. L.; Jia, X.; Tonelli, A. E. *J. Polym. Sci. B, Polym. Phys.* **2005**, *43*, 2086−2096.
(34) The crystalline region of β-CD⊃**1** is too small to be observed by solid-state NMR.

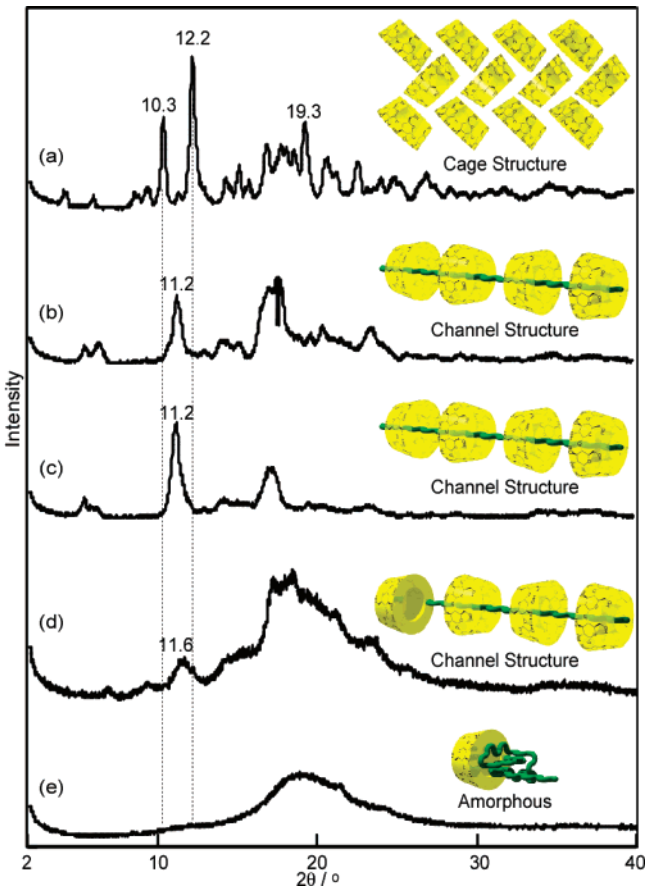

Figure 2. X-ray powder diffraction patterns for β-CD (a), β-CD⊃poly(ϵ-caprolactone) (b), β-CD⊃poly(propylene glycol) (c), β-CD⊃**1** (d), and **1** (e).

chain in β-CD⊃**1** is arranged linearly in the β-CD channel structure to prevent the random coil conformation.

Structures of CDs⊃1 and 1 in Bulk. X-ray powder diffraction measurements were carried out to investigate the structures of β-CD⊃**1** and **1** (Figure 2). β-CD showed characteristic diffraction peaks ($2\theta = 10.3°$ and 12.2°, Figure 2a). On the other hand, poly-*pseudo*-rotaxanes (β-CD⊃poly(ϵ-caprolactone) and β-CD⊃poly(propylene glycol)) showed a characteristic single peak ($2\theta \approx 11°$, Figure 2b,c). The structures of β-CD and β-CD⊃poly(propylene glycol) are cage-type and channel-type, respectively, which were revealed by the single-crystal X-ray analysis.[19,20,35] It should be noted that β-CD⊃**1** showed a single peak around $2\theta \approx 11°$, characteristic for the channel-type structure (Figure 2d), whereas the purified **1** showed only a broad peak but did not show any sharp diffraction peaks (Figure 2e). These results indicate that β-CD⊃**1** and **1** form poly-*pseudo*-rotaxane and amorphous regions, respectively.

Figure 3 shows proposed structures of **1** and β-CD⊃**1** to demonstrate the differences in the polymerization activity. The polymer chain of **1**, which forms a random coil conformation in the amorphous state, has a lower mobility affected by inter- or intrapolymer chain interactions. It is difficult for new monomers to approach the active site of β-CD at the end of **1** due to the presence of the polymer chain, and the β-CD moiety at the end of **1** has no ability to include a new δ-VL molecule.[36] In the poly-*pseudo*-rotaxane β-CD⊃**1**, however, CDs threaded onto the polymer chain were supposed to prevent the polymer chain from forming a random coil conformation (Figure 3b). The included polyester chain with higher mobility moves along the channel to clear the β-CD at the end of β-CD⊃**1** in the propagation step. Another new δ-VL is accessible to the β-CD at the end of polymer chain. The included δ-VL is supposed to be inserted at the ester bond between β-CD and the polymer chain.[37] The polymer chain elongates with the higher mobility in the β-CD channel.

Conclusion

We found that the polymer chain of **1** was propagated by the formation of poly-*pseudo*-rotaxane structure (CDs⊃**1**), which was necessary to initiate further polymerization of lactone in the solid state. β-CD at the end of CDs⊃**1** is the active site for the polymerization of δ-VL. Furthermore, CDs threaded onto **1** also play another essential role, preventing the polymer chain from getting entangled with itself or another polymer chain so as to keep the propagating state of the polyester. These processes are similar to those of chaperone proteins in biological systems, which assist protein folding and allow the functional state of proteins. CDs showed not only the activation and transformation of monomer like an enzyme, but also protein-like refolding activity as an artificial chaperone. This is the first study on a supramolecular catalyst, poly-*pseudo*-rotaxane with an axis extensible by the polymerization. The applications of this system are now under investigation.

Experimental Section

Measurements of Poly(δ-VL)s by Solid-State ^{13}C MAS/NMR. ^{13}C 1pda/MAS NMR (single pulse with ^{1}H decoupling /MAS NMR) spectra were recorded at 75.6 MHz in a solid state on a Chemagnetics JNM-CMX300W spectrometer with a sample spinning rate of 4.0 kHz at 30−100 °C. In the 1pda technique, the nuclear Overhauser effect (NOE) is used to enhance the ^{13}C signal by saturating the proton resonances (compare to the cross polarization (CP) technique). The chemical shifts of the mobile regions in a polymer can be obtained by using 1pda/MAS NMR. Spin−lattice relaxation time data were obtained with the CP−T_1 pulse sequence.

Preparation of 2-*O*-Poly(δ-VL)-β-CD (1). β-CD (2.27 g, 2.00 mmol) was dried in vacuo at 80 °C for 24 h. δ-VL (0.927 mL, 10.0 mmol) was then added to β-CD under an argon atmosphere. The reaction tube was sealed under an argon atmosphere, and the heterogeneous mixture was kept at 100 °C with stirring. After 48 h, the polymerization was terminated by washing with water. The resulting powder was dissolved in DMF (25 mL). The resultant polymer solution was added to THF (250 mL) to precipitate β-CD. The precipitated β-CD was removed by centrifugation, and the filtrate was evaporated in vacuo to remove the excess lactone and the solvents. 2-*O*-poly(δ-VL)-β-CD was obtained in 97% yield. ^{1}H NMR (DMSO-d_6, 30 °C, 500 MHz): δ 5.65 (br, 13H, $O_{2,3}H$), 4.82 (br, 6H, C_1H), 4.39 (br, 7H, O_6H), 4.29 (br, 1H, C_1'H), 4.12 (br, 1H, C_2'H), 3.97 (br, 38H, δ-polymer), 3.82 (br, 1H, C_3'H), 3.63 (br, 20H, $C_{6,3}H$), 3.55 (br, 7H, C_5H), 3.34 (br, 15H, $C_{4,2}H$ and δ-polymer (hydroxyl terminal moiety)), 2.28 (br, 40H, α-polymer), 1.54 (br, 78H, β- and δ-polymer), 1.39(m, 2H, β-polymer

(35) Udachin, K. A.; Wilson, L. D.; Ripmeester, J. A. *J. Am. Chem. Soc.* **2000**, *122*, 12375−12376.

(36) The mixture of β-CD and δ-VL gave **1** as reported in ref 29. The resulting polymer **1**, which was washed with only water to remove free β-CD, was found to form poly-*pseudo*-rotaxane (β-CD⊃**1**) by powder X-ray diffraction analysis. This result indicates that **1** prepared from the mixture of β-CD and δ-VL forms the poly-*pseudo*-rotaxane structure during the polymerization.

(37) To confirm the insertion of monomer between β-CD and the polymer chain, block-copolymerization was carried out by using β-butyrolactone (β-BL) and β-CD⊃**1**. Poly(β-BL) was inserted between the β-CD−polymer linkage (see Supporting Information).

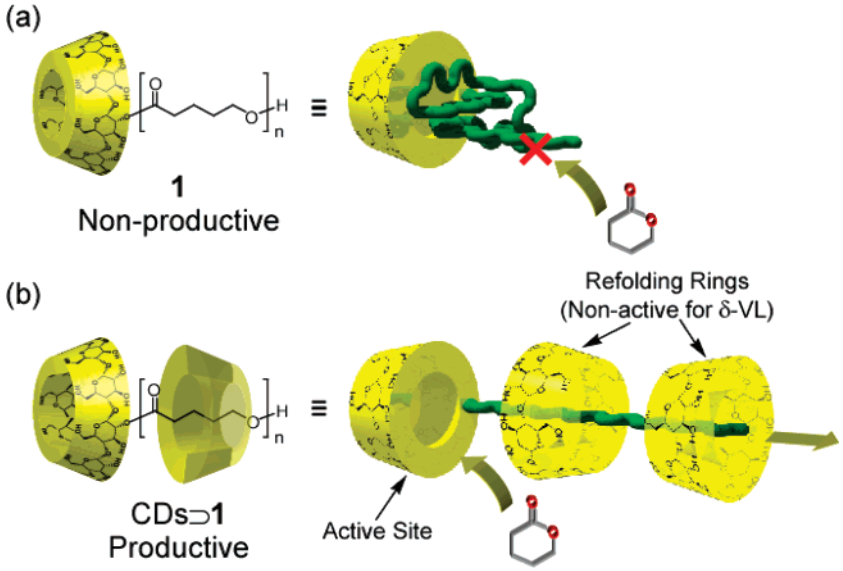

Figure 3. Schematic representations of the mechanism for reinitiating the polymerization of δ-VL by **1** or CDs⊃**1** in bulk at 100 °C.

(hydroxyl terminal moiety)). ^{13}C NMR (DMSO-d_6, 30 °C, 125 MHz): δ 174.4 (carbonyl-polymer (carboxyl terminal moiety)), 173.0 (carbonyl-polymer (hydroxyl terminal moiety)), 172.7 (carbonyl-polymer), 102.6 (C_1'), 102.1 (C_1), 82.4 (C_4'), 81.7 (C_4), 73.2 (C_3), 72.6 (C_2), 72.2 (C_5), 69.1 (C_3'), 63.4 (δ-polymer and C_2'), 60.4 (δ-polymer (hydroxyl terminal moiety)), 60.1(C_6), 59.7 (C_6'), 33.4 (α-polymer (carboxyl terminal moiety)), 33.1 (α-polymer), 31.9 (γ-polymer (hydroxyl terminal moiety)), 27.7 (γ-polymer), 21.3 (β-polymer (carboxyl terminal moiety)), 21.1 (β-polymer). IR (KBr): 3409, 2957, 1731, 1643 cm^{-1}.

Preparation of β-CD⊃2-*O*-poly(δ-VL)-β-CD Inclusion Complex (β-CD⊃1). β-CD (4.54 g, 4.00 mmol) was dissolved in 30 mL of water. 2-*O*-Poly(δ-VL)-β-CD (0.627 g, 0.20 mmol) was added to the solution. The solution became gradually turbid. After vigorous stirring for 48 h, the white powder of the β-CD⊃2-*O*-poly(δ-VL)-β-CD was collected by centrifugation and dried in vacuo at 50 °C (yield 82%). ^{1}H NMR (DMSO-d_6, 30 °C, 500 MHz): δ 5.66 (br, 209H, O2,3H), 4.83 (br, 104H, C_1H), 4.40 (br, 210H, O_6H), 4.29 (br, 1H, $C_1'H$), 4.12 (br, 1H, $C_2'H$), 3.97 (br, 38H, δ-polymer), 3.82 (br, 1H, $C_3'H$), 3.63 (br, 314H, $C_{6,3}H$), 3.55 (br, 105H, C_5H), 3.34 (br, 211H, $C_{4,2}H$ and δ-polymer (hydroxyl terminal moiety)), 2.28 (br, 40H, α-polymer), 1.54 (br, 78H, β- and δ-polymer), 1.39(m, 2H, β-polymer (hydroxyl terminal moiety)). ^{13}C NMR (DMSO-d_6, 30 °C, 125 MHz): δ 174.4 (carbonyl-polymer (carboxyl terminal moiety)), 173.0 (carbonyl-polymer (hydroxyl terminal moiety)), 172.7 (carbonyl-polymer), 102.6 (C_1'), 102.1 (C_1), 82.4 (C_4'), 81.7 (C_4), 73.3 (C_3), 72.6 (C_2), 72.3 (C_5), 69.1 (C_3'), 63.4 (δ-polymer and C_2'), 60.4 (δ-polymer (hydroxyl terminal moiety)), 60.2-(C_6), 59.7 (C_6'), 33.4 (α-polymer (carboxyl terminal moiety)), 33.1 (α-polymer), 31.9 (γ-polymer (hydroxyl terminal moiety)), 27.7 (γ-polymer), 21.3 (β-polymer (carboxyl terminal moiety)), 21.1 (β-polymer).

Preparation of α-CD⊃2-*O*-Poly(δ-VL)-β-CD inclusion complex (α-CD⊃1). α-CD (3.89 g, 4.00 mmol) was dissolved in 30 mL of water. 2-*O*-Poly(δ-VL)-β-CD (0.627 g, 0.20 mmol) was added to the solution. The solution became gradually turbid. After vigorous stirring for 48 h, the white powder of the α-CD⊃2-*O*-poly(δ-VL)-β-CD was collected by centrifugation and dried in vacuo at 50 °C (yield 76%). ^{1}H NMR (DMSO-d_6, 30 °C, 500 MHz): δ 5.65 (br, 13H, $O_{2,3}$H-β-CD), 5.47 (d, 168H, O_2H-α-CD), 5.41 (d, 84H, O_3H-α-CD), 4.82 (br, 6H, C_1H-β-CD), 4.77 (d, 84H, C_1H-α-CD), 4.44 (t, 91H, O_6H-CDs), 4.29 (br, 1H, C_1'H-β-CD), 4.12 (br, 1H, C_2'H-β-CD), 3.97 (br, 38H, δ-polymer), 3.82 (br, 1H, C_3'H-β-CD), 3.63 (m, 363H, $C_{3,6,5}H$-CDs), 3.34 (br, 221H, $C_{4,2}H$-CDs and δ-polymer (hydroxyl terminal moiety)), 2.28 (br, 40H, α-polymer), 1.54 (br, 78H, β- and δ-polymer), 1.39(m, 2H, β-polymer (hydroxyl terminal moiety)). ^{13}C NMR (DMSO-d_6, 30 °C, 125 MHz): δ 174.4 (carbonyl-polymer (carboxyl terminal moiety)), 173.0 (carbonyl-polymer (hydroxyl terminal moiety)), 172.7 (carbonyl-polymer), 102.1 (C_1-CDs), 82.1 (C_4-CDs), 73.3 (C_3-CDs), 72.2 ($C_{2,5}$-CDs), 69.1 (C_3'-β-CD), 63.4 (δ-polymer and C_2'-CDs), 60.4 (δ-polymer (hydroxyl terminal moiety)), 60.1(C_6-CDs), 33.4 (α-polymer (carboxyl terminal moiety)), 33.1 (α-polymer), 31.9 (γ-polymer (hydroxyl terminal moiety)), 27.7 (γ-polymer), 21.3 (β-polymer (carboxyl terminal moiety)), 21.1 (β-polymer).

Preparation of β-CD⊃2-*O*-Poly(δ-VL)-β-CD⊃Adamantane Inclusion Complex (β-CD⊃1⊃Ad). Adamantane (0.136 g, 1.00 mmol) and β-CD⊃2-*O*-poly(δ-VL)-β-CD (1.54 g, 0.20 mmol) were added to 80 mL of water. After the mixture was stirred for 48 h, the white precipitate was collected by centrifugation, washed with 40 mL of water twice, and dried in vacuo to remove free adamantane with sublimation (yield 56%). ^{1}H NMR (DMSO-d_6, 30 °C, 500 MHz): δ 5.66 (br, 195H, $O_{2,3}H$), 4.83 (br, 97H, C_1H), 4.40 (br, 98H, O_6H), 4.29 (br, 1H, $C_1'H$), 4.12 (br, 1H, $C_2'H$), 3.97 (br, 38H, δ-polymer), 3.82 (br, 1H, $C_3'H$), 3.63 (br, 293H, $C_{6,3}H$), 3.55 (br, 98H, C_5H), 3.34 (br, 197H, $C_{4,2}H$ and δ-polymer (hydroxyl terminal moiety)), 2.28 (br, 40H, α-polymer), 1.85 (m, 4H, methine of adamantane), 1.71 (t, 12H, methylene of adamantane), 1.54 (br, 78H, β- and δ-polymer), 1.39(m, 2H, β-polymer (hydroxyl terminal moiety)). ^{13}C NMR (DMSO-d_6, 30 °C, 125 MHz): δ 174.4 (carbonyl-polymer (carboxyl terminal moiety)), 173.0 (carbonyl-polymer (hydroxyl terminal moiety)), 172.7 (carbonyl-polymer), 102.6 (C_1'), 102.1 (C_1), 82.4 (C_4'), 81.7 (C_4), 73.3 (C_3), 72.6 (C_2), 72.3 (C_5), 69.1 (C_3'), 63.4 (δ-polymer and C_2'), 60.4 (δ-polymer (hydroxyl terminal moiety)), 60.2(C_6), 59.7 (C_6'), 37.4 (methine of adamantane), 33.4 (α-polymer (carboxyl terminal moiety)), 33.1 (α-polymer), 31.9 (γ-polymer (hydroxyl terminal moiety)), 27.7 (γ-polymer), 27.5 (methylene of adamantane), 21.3 (β-polymer (carboxyl terminal moiety)), 21.1 (β-polymer).

Postpolymerization of δ-VL initiated by β-CD⊃1 in bulk. All the postpolymerizations of lactones by CD⊃2-*O*-poly(δ-VL)-β-CD were carried out by the following method. β-CD⊃2-*O*-poly(δ-VL)-β-CD (7.68 g, 1.00 mmol) was dried in vacuo at 80 °C for 24 h. δ-VL (1.86 mL, 20.0 mmol) was then added to β-CD under an argon atmosphere. The reaction tube was sealed under an argon atmosphere, and the heterogeneous mixture was kept at 100 °C with stirring. After 48 h, the polymerization was terminated by adding a large amount of dry DMF (25 mL). The resulting powder was dissolved in DMF. The resultant polymer solution was added to THF (250 mL) to precipitate β-CD. The precipitated β-CD was removed by centrifugation, and the

filtrate was evaporated in vacuo to remove the excess lactone and the solvents. 2-*O*-poly(δ-VL)-β-CD was obtained (conversion of δ-VL, 76%)

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Supporting Information Available: Detailed experimental procedures, GPC diagrams of the products, MALDI-TOF mass spectrum of the product, and block copolymerization using β-CD$\supset$**1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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