Supporting Information for

Formation of Reactant Complex Structure for Initiation Reaction of Lactone Ring-Opening Polymerization by Cooperation of Multiple Cyclodextrin

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Full reference for the main text

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DFT Calculations for Ring-Opening Reaction Mechanisms

To predict the mechanism of the VL ring-opening reaction catalyzed by β-CD, we carried out QM calculations. We employed a model system that consists of two ethanol (one for hydrogen bonding and another for nucleophilic attack) and one VL molecules. Since the atomic charges of OH groups of ethanol (-0.607*e* and 0.374*e* for O and H atom, respectively) and glucose molecules (-0.620*e* and 0.423*e* at the C2 position, -0.619*e* and 0.438*e* at the C3 position, and -0.583*e* and 0.402*e* at the C6 position) are similar, we assume the OH groups of the ethanol molecules mimic those of GL units of β-CD. Here, the atomic charges were calculated by the Merz-Singh-Kollman scheme at the B3LYP/6-31G(d,p) level of DFT calculations at the optimized structure in vacuum.

All the QM calculations were executed by Gaussian 09 program package. Density functional theory (DFT) calculations of the model system at the M06-2X/6-31G(d,p) level were carried out in gas phase. The reactions were analyzed as the following procedure. First, transition state (TS) structures were optimized using the keyword “opt=TS”. Then, the structures of the reactant and product were optimized after intrinsic reaction coordinate (IRC) calculation from the TS structure and the energy barriers were calculated. Finally, we obtained TS, reactant, and product structures on two reaction pathways.

To elucidate the reaction mechanism of the VL ring-opening reaction catalyzed by β-CD, we assumed two reaction schemes of Nu attack 1 and 2 (Figure 3). Nu attack 1 is based on the mechanism described by Harada et al[1]. In this scheme, a hydrogen atom of OH group at the C2 position of β-CD approaches to the ester O_E of the VL directly. Nu attack 2 proceeds via a hemiacetal intermediate. The hemiacetal formation is produced by moving the hydrogen atom of OH group to the O_C atom of the VL. This mechanism has been shown by QM calculations of a ε-caprolactone ring-opening reaction catalyzed by sulfonic acids.[2]

Energy diagrams of Nuclear attack 1 and 2 were calculated by QM calculations. Instead of the whole VL/β-CD inclusion complex, the model system consists of one VL molecule and two ethanol molecules. The reaction pathways were investigated by calculation of the TS followed by reactant and product structure optimizations after IRC calculations. The energy diagram of each reaction pathway are shown in Figure S3 and S4.

First, we explain the results of Nu attack 1. The hydrogen atom of the OH group at the C2 position approaches to the O_E atom of the VL and results in the ring-opening of VL directly. We found a TS structure (TS1 in Figure S3) between the reactant (Reactant1) and product (Product1) structures for this pathway. The O_2-C_C distance for the nucleophilic attack of TS1 was 1.626 Å. The reaction barrier was 41.4 kcal/mol.

Next, we show the results of Nu attack 2. By searching the TS structure with the condition of the hydrogen atom of the OH group approaches to the O_C atom of the VL to form the hemiacetal intermediate, we obtained the TS (TS2 in Figure S4) between the reactant (Reactant2) and hemiacetal intermediate (Intermediate) structures. The O_2-C_C distance for the nucleophilic attack of TS2 is 1.708 Å. Next, we searched and obtained the second TS (TS3) between the hemiacetal intermediate and product (Product2) structures to move the hydrogen atom from the hemiacetal to the O_E atom of the VL for the ring-opening reaction. In TS3, the hydrogen atom is at a position with a similar distance (1.26 and 1.19 Å) from both the carbonyl and the ester oxygen atoms. As described above, we found the two kinds of VL ring-opening reaction pathways by the nucleophilic attack of OH groups. The reaction barriers for the first hemiacetal intermediate formation and second ring-opening reactions are 37.7 and 34.2 kcal/mol, respectively.

The DFT calculations of the model system gave the two reaction pathways (Nu attack 1 through the direct ring-opening and Nu attack 2 through the hemiacetal intermediate) with the almost same reaction barrier about 40 kcal/mol. This result indicates that both of the reaction pathways can be the VL ring-opening mechanism starting from the VL/β-CD inclusion complex. Therefore, we investigate the reactant complex structures by assuming both the Nu attack 1 and 2 for the nucleophilic attack condition.

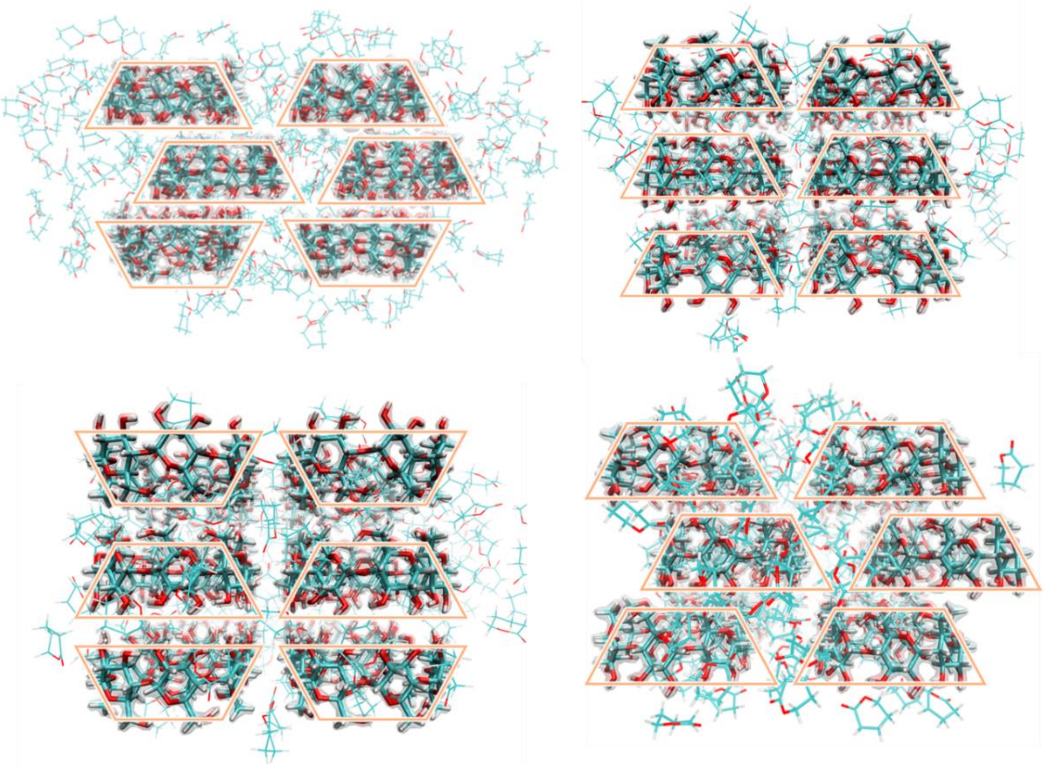

Figure S1. Four initial snapshots of model 2. Atoms of the β-CDs and VLs are drawn by thick lines and thin lines, respectively. β-CD frameworks are drawn with orange trapezoids for better visualization.

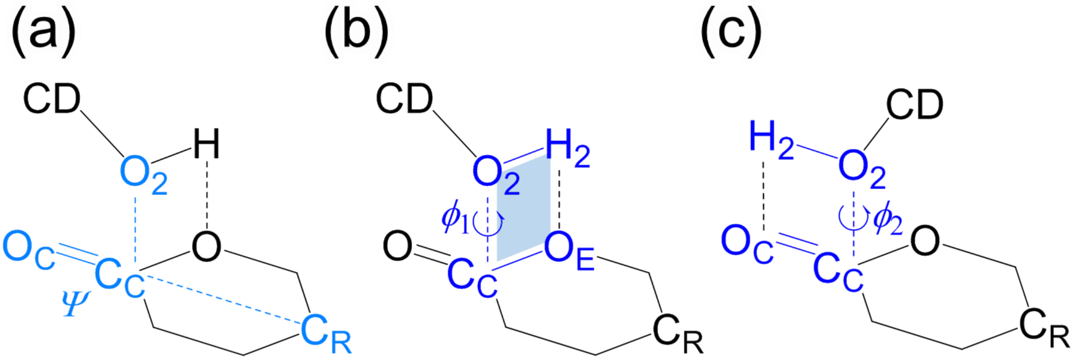

Figure S2. Definitions of Ψ, ϕ_1, and ϕ_2 for nucleophilic attack conditions.

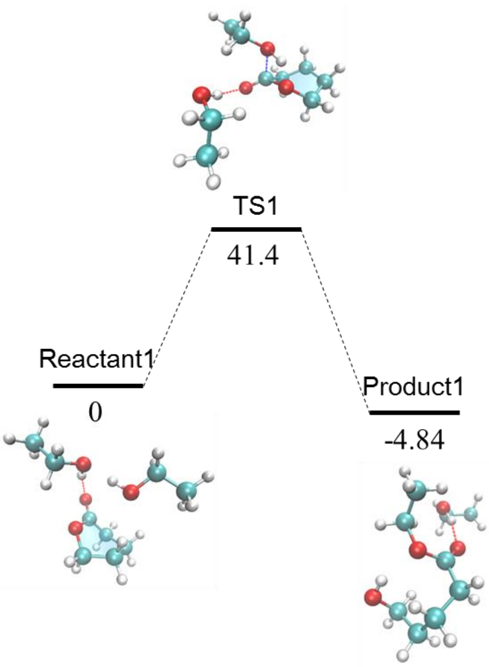

Fig.S3. Energy profile for the ring-opening reaction of VL by two ethanol molecules by Nu attack 1 pathway calculated by the DFT calculations at M06-2X/6-31G(d,p) level. Energy of each structure is shown in kcal/mol.

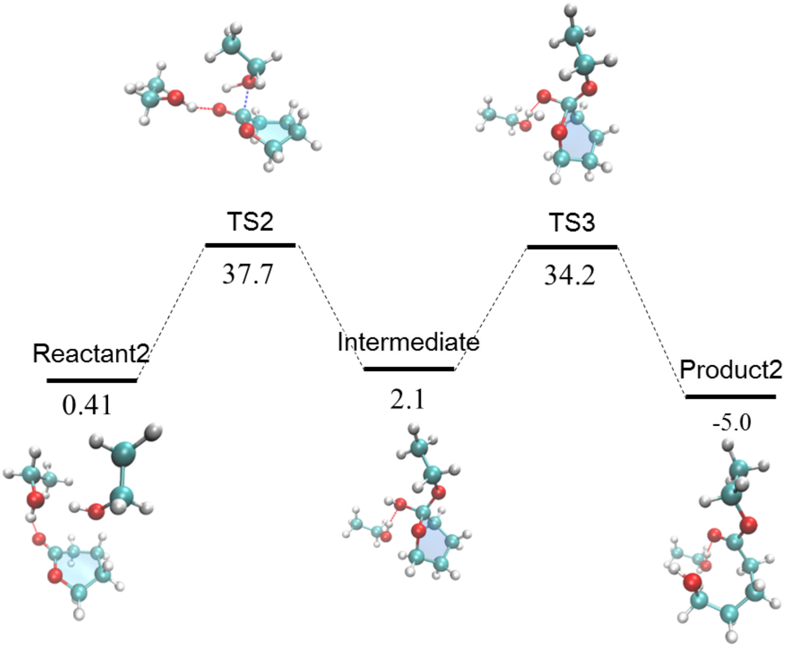

Fig.S4. Energy profile by Nu attack 2 pathway.

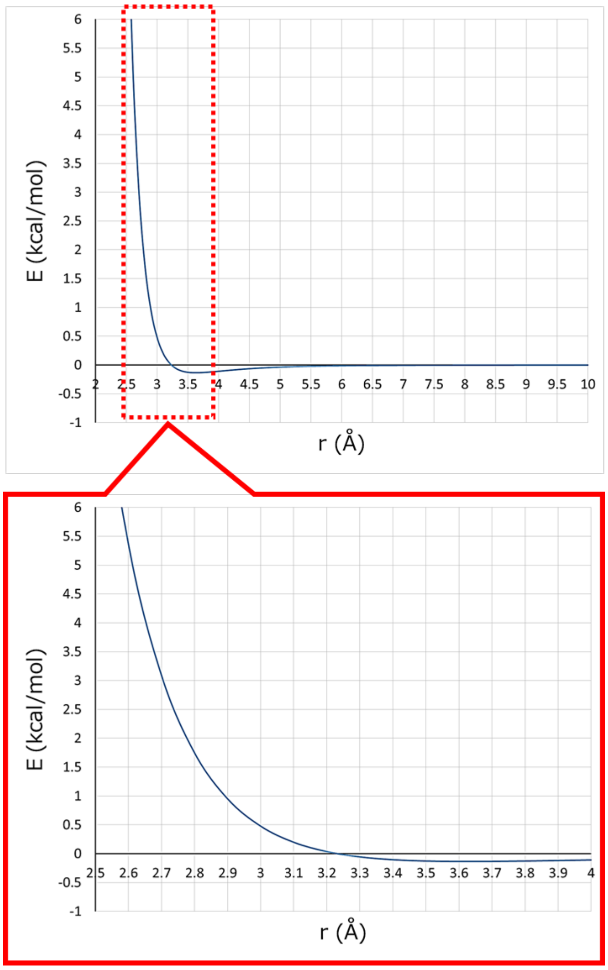

Figure S5. LJ parameter term between O_2 and Cc (equilibrium distance 3.629 Å and potential well depth 0.1345 kcal/mol).

References

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