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Supporting Information for:

Supramolecular effects on formation of $CaCO_3$ thin films on a polymer matrix

Fangjie Zhu, Tatsuya Nishimura,* Hiroki Eimura, and Takashi Kato*

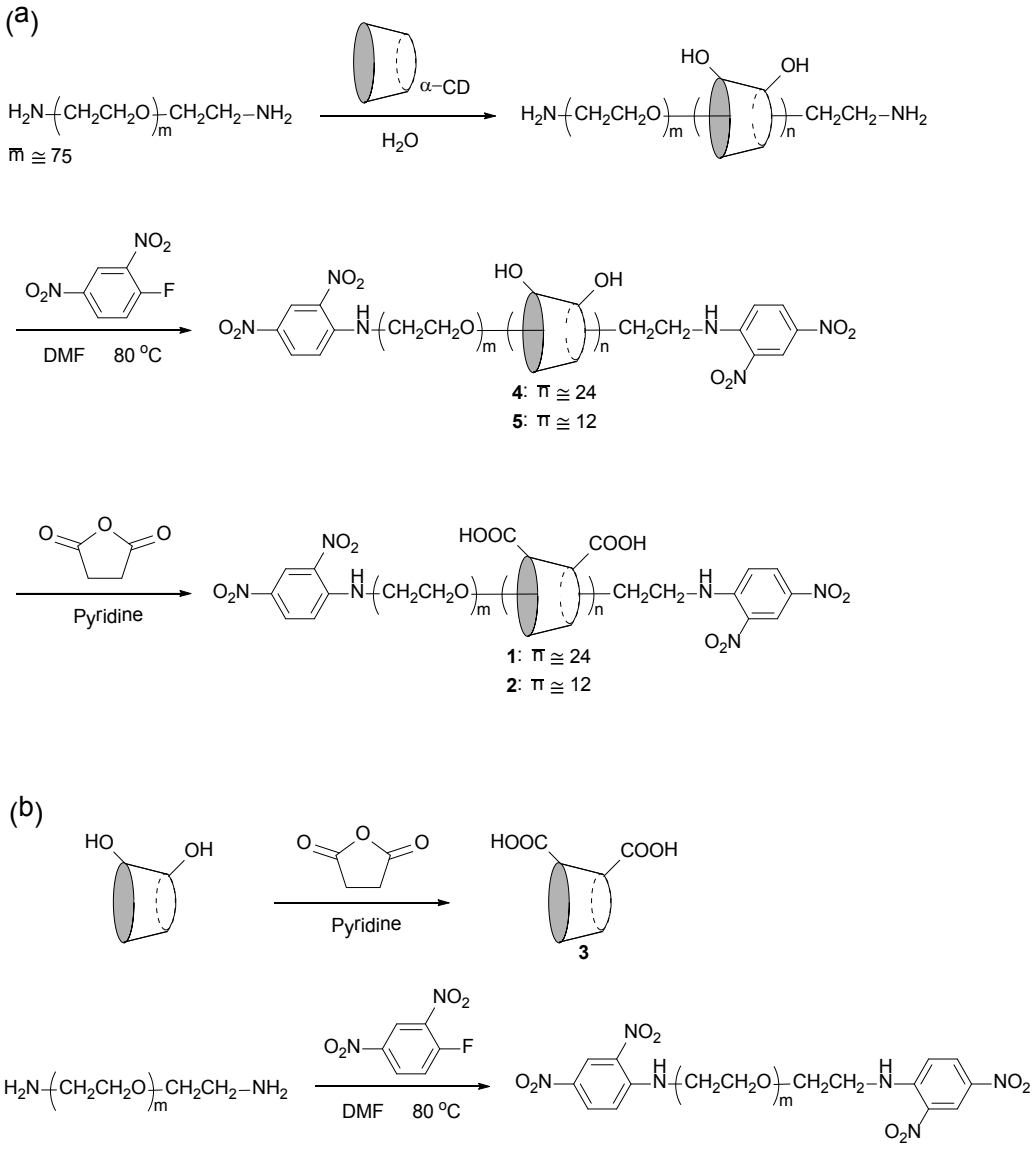
Department of Chemistry and Biotechnology, School of Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan.

E-mail: tatsuya@chembio.t.u-tokyo.ac.jp; kato@chiral.t.u-tokyo.ac.jp

Experimental Section

Synthesis of Carboxylated Polyrotaxanes

Carboxylated polyrotaxanes **1** and **2** were synthesized according to previously reported methods.[1,2] As shown in Scheme S1a, simple polyrotaxanes **4** and **5** consisting of α-CD, PEG, and capped by 2,4-dinitrofluorobenzene were first synthesized. They were subsequently modified with carboxyethylester groups to give polyrotaxanes **1** and **2**. The carboxylated α-CD (α-CD-COOH, **3**) and the capped PEG were also synthesized (Scheme S1b).



Scheme S1 Schematic representation of the syntheses of carboxylated polyrotaxanes (**1** and **2**) (a), α-CD-COOH (**3**) (b), and capped PEG (b).

Materials

α-Cyclodextrin (α-CD) and 2,4-dinitrofluorobenzene were obtained from Tokyo Chemical Industry, Co., Ltd (Tokyo, Japan). Bis(2-aminoethyl)poly(ethylene glycol) (average MW: 3350) was obtained from Sigma-Aldrich (St. Louis, USA). Succinic anhydride and the solvents were purchased from Wako (Tokyo, Japan). D_2O used as the solvent for NMR were obtained from Acros Organics (New Jersey, USA). Poly(vinyl alcohol) (PVA) (87–89% hydrolyzed, $\overline{M}_w$: 1.5×10^5 to 1.9×10^5) was purchased from Sigma-Aldrich (St. Louis, USA). Calcium chloride and ammonium carbonate were purchased from Wako (Tokyo, Japan). All reagents were of the highest grade and used without further purification.

Synthesis of Polyrotaxanes Consisting of PEG and α-CD (4 and 5)

The simple polyrotaxanes before carboxylation (**4** and **5**, Scheme S1) were prepared according to the previously reported method by Harada.[1] To synthesize polyrotaxanes **4**, bis(2-aminoethyl)poly(ethylene glycol) (120 mg, 3.58×10^{-5} mol) and α-CD (2.2 g, 2.26×10^{-3} mol) were dissolved in water (13.5 mL). The mixture of them was irradiated with ultrasonic waves for 10 min, and allowed to stand overnight. The precipitation was then freeze-dried and vacuum-dried at 60 °C to obtain the pseudopolyrotaxane (2.32 g). Next, 2,4-dinitrofluorobenzene (1.92 g, 1.03×10^{-2} mol) was used to react with the pseudopolyrotaxane in DMF (8 mL). The mixture was stirred under argon atmosphere overnight at r.t., and stirred at 80 °C for 3 hours. The mixture was then cooled and dropwisely added into acetone. The precipitate was collected by centrifugation. The precipitate was then dissolved in DMSO and poured into methanol (three times), and into water (three times). The resultant precipitate was collected and dried under vacuum to give polyrotaxane **4** (174 mg, 18 %). ^{1}H NMR (D_2O/NaOD (10 mM), 400 MHz): δ 9.14 (*meta* H of phenyl), 8.33 (*meta* H of phenyl), 7.19 (*ortho* H of phenyl), 5.01 (1-H of α-CD), 4.1–3.3 (2,3,4,5,6-H of α-CD and CH_2 of PEG), 3.69 (CH_2 of PEG).

In the synthesis of polyrotaxane **5**, bis(2-aminoethyl)poly(ethylene glycol) (120 mg, 3.58×10^{-5} mol) and α-CD (0.73 g, 7.50×10^{-4} mol) were mixed in water (4.5 mL) to prepare the pseudopolyrotaxane. The same procedures as in the synthesis of **4** were then followed to give **5** (84 mg, 16%).

Functionalization of Polyrotaxanes and α-CD with Carboxyethylester Groups (1, 2, and 3)

The functionalization of polyrotaxanes and α-CD was carried out according to the reported procedures.[2] Succinic anhydride (2.63 g, 2.63×10^{-2} mol) and **4**, **5**, or α-CD (300 mg, *ca.* 1.85×10^{-3} mol as hydroxyl group) were added into pyridine (12.5 mL). After stirring for 1 day (2 hours for the synthesis of **3**) at r.t., the mixture was poured into excess tetrahydrofuran (THF). The precipitate was thoroughly washed with acetone and dried in vacuum, to give **1** (0.33 g, 65%), **2** (0.32g, 63%), and **3** (0.4 g, 77%). ^{1}H NMR of **1** and **2** (D_2O/Na_2CO_3 (10 mM), 400 MHz): δ 9.06 (*meta* H of phenyl), 8.30 (*meta* H of phenyl), 7.18 (*ortho* H of phenyl), 4.9–5.3 (1-H of α-CD), 4.5–3.5 (2,3,4,5,6-H of

α-CD and CH_2 of PEG), 3.68 (CH_2 of PEG), 2.8–2.3 (CH_2 of carboxyethylester). ^{1}H NMR of **3** (D_2O/Na_2CO_3 (10 mM), 400 MHz): 5.02 (1-H of α-CD), 4.5–3.5 (2,3,4,5,6-H of α-CD), 2.8–2.5 (CH_2 of carboxyethylester).

Synthesis of a Capped PEG

PEG capped with 2,4-dinitrofluorobenzene was prepared according to the previously reported method[1] with slight modification. Bis(2-aminoethyl)poly(ethylene glycol) (120 mg, 3.58×10^{-5} mol) and 2,4-dinitrofluorobenzene (1.92 g, 1.03×10^{-2} mol) were dissolved into DMF (8 mL). The mixture was stirred under argon atmosphere overnight at r.t., and stirred at 80 °C for 6 hours. The mixture was then cooled and added into a mixture of hexane and ethyl acetate (7:3 v/v). The precipitate was collected and thoroughly washed with hexane, and dried under vacuum to give capped PEG (40 mg, 30%). ^{1}H NMR (D_2O, 400 MHz): δ 9.04 (1H, *meta* H of phenyl), 8.24 (*meta* H of phenyl), 7.15 (*ortho* H of phenyl), 4.09 (-NH-C*H*$_2$-), 3.85–3.35 (CH_2 of PEG).

Preparation of PVA Matrices

PVA matrices were obtained by spin coating of a DMSO solution of PVA (4 wt. %, 400 μL) onto glass substrates. The matrices were then air-dried and annealed at 180 °C for 10 min.

Crystallization of $CaCO_3$

Purified water obtained from an Auto Pure WT100 system (Yamato, Tokyo, Japan) was used for crystallization. The procedure for crystal growth of $CaCO_3$ was employed according to previously reported method.[3,4] As shown in Fig. S1, aqueous solutions of $CaCl_2$ ([Ca^{2+}] = 10 mM) containing **1** or **2** (1 mg mL^{-1}), or containing **3** (1 mg mL^{-1}) and capped PEG (0.1 mg mL^{-1}) were transferred into vessels containing the PVA matrix. The vessels were then placed in a closed desiccator together with a vial containing $(NH_4)_2CO_3$. An FMU-131I incubator (Fukushima, Tokyo, Japan) was employed to maintain the temperature constant for crystallization (25 °C). Crystallization was carried out for 1 day. The samples obtained were then taken out of the solution and dried for characterization.

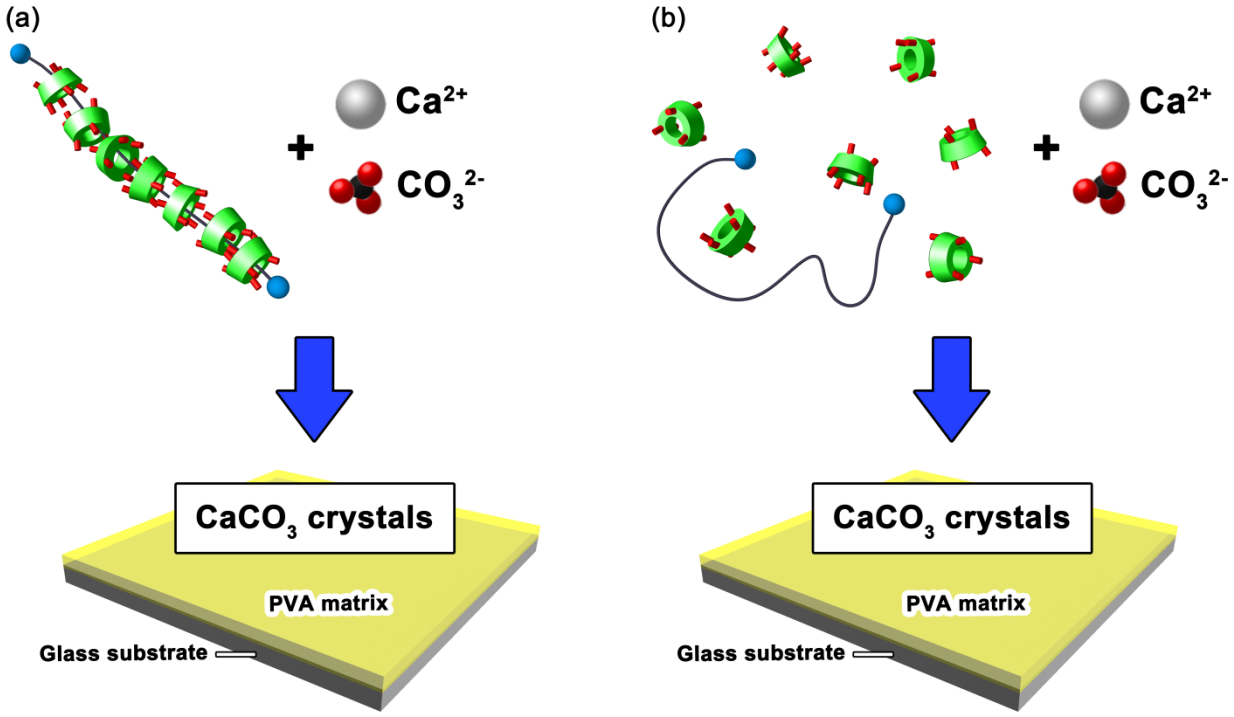


Fig. S1 Schematic representation of $CaCO_3$ crystallization in the presence of (a) carboxylated polyrotaxane and (b) mixture of α-CD-COOH and the capped PEG.

Measurements

Size exclusion chromatography (SEC) was carried out using a HPLC system (Jasco, Tokyo, Japan) equipped with a UV-vis detector (360 nm) and a refractive index detector. The TSKgel G5000PW$_{XL}$ column and the G3000PW column (Tohso, Tokyo, Japan) were used. The Na_2CO_3 aqueous solution (10 mM) was used as solvent. ^{1}H NMR spectra were recorded on a JNM-LA400 spectrometer (JEOL, Tokyo, Japan) using D_2O as a solvent. Chemical shifts were referenced to the solvent residual peak (δ 4.79 ppm). 2D-NOESY experiment was carried out at 30 °C. The mixing time for NOESY measurement was 100 ms. The 1024 experiments were carried out with eight scans per experiment. Mass spectra for **1** and **2** were obtained by a Autoflex Speed™ spectrometer (Bruker, Karlsruhe, Germany), using the matrix prepared from 2',4',6'-trihydroxyacetophenone and 1,1,3,3-tetramethylguanidine.[5] Samples of $CaCO_3$ crystals were platinum-coated using a Hitachi E-1030 ion sputter (Hitachi, Tokyo, Japan) for SEM observation. SEM images were obtained by using a Hitachi S-4700 field-emission SEM (Hitachi, Tokyo, Japan). TEM images were taken with a JEOL JEM-2010HC operated at 200 kV. Polarizing optical micrographs were obtained with an Olympus BX51 polarizing optical microscope (Olympus, Tokyo, Japan). Fourier transform infrared (FTIR) spectra were collected by a Jasco FT/IR-660 Plus spectrometer (Jasco, Tokyo, Japan) using

KBr pellets. Raman spectra over the spectral range of 150–1200 cm^{-1} was obtained using a Jasco NRS-1000 micro-Raman system (Jasco, Tokyo, Japan), with the excitation wavelength of 514 nm.

2D NOESY NMR Spectrum of 4

Fig. S2 shows the 2D NOESY NMR spectrum of **4**, signals of 3-H and 5-H of α-CD were observed to correlate with the resonance of the CH_2 of PEG. This observation indicates the formation of polyrotaxane structure.

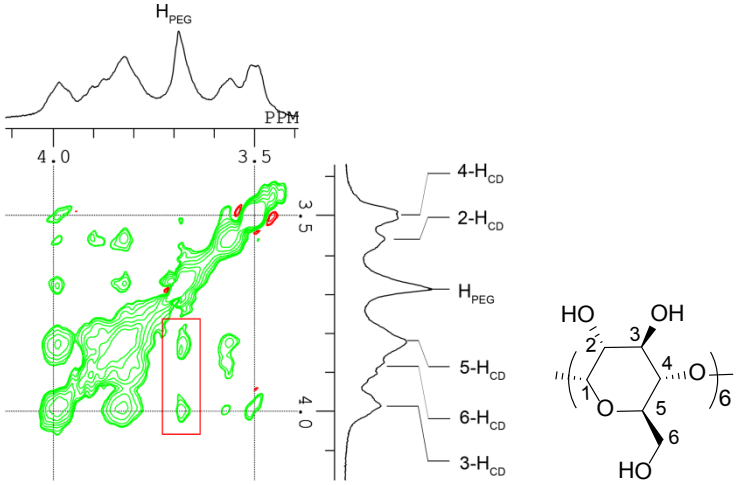


Fig. S2 A part of 2D NOESY NMR spectrum of **4** in D_2O solution of NaOD (10 mM) at 30 °C.

Estimation of Molecular Weight of Polyrotaxanes and Substitution Degree of Carboxyethylester Group

Fig. S3 presents the NMR spectra of compounds **1**, **2**, and **3** hydrolyzed by NaOD. Molecular weights of the polyrotaxanes and substitution degrees of the carboxyethylester group were estimated from these spectra. The PEG chains in the polyrotaxanes have a known average molecular weight of 3350. Therefore, by comparing the integrations over the ranges of 4.95–4.85 (1-H of α-CD) and 3.75–3.65 (CH_2 of PEG), the numbers of α-CDs per polyrotaxane were estimated as 23.8 (**1**) and 12.3 (**2**). As a single cavity of α-CD approximately accommodates two ethylene glycol units,[6] the coverage of PEG chains was estimated as 63% (**1**) and 32% (**2**). By comparing the integrations over the ranges of 4.95–4.85 (1-H of α-CD) and 2.46–2.36 (CH_2 of carboxyethylester), the substitution degrees of carboxyethylester group per α-CD were estimated as 7.1 (**1**), 7.5 (**2**), and 6.9 (**3**).

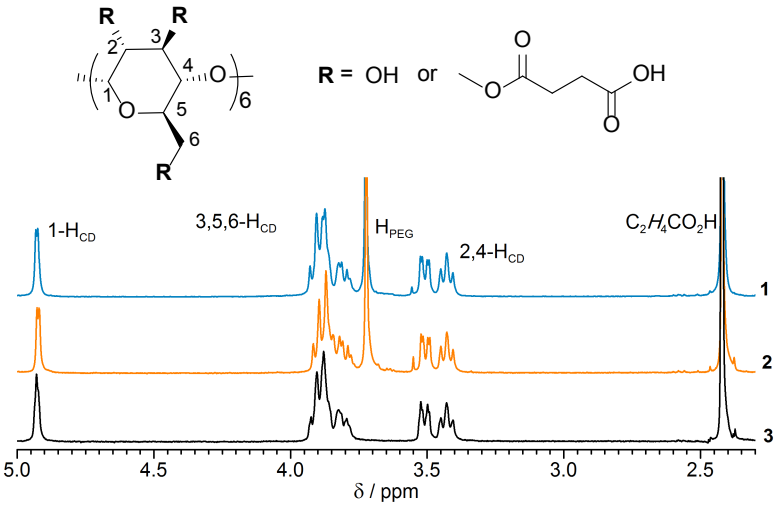


Fig. S3 400 MHz ^{1}H NMR spectrum of **1**, **2**, and **3** in D_2O solution of NaOD (1M).

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