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Supplementary Information

Significant Impact of Host-Guest Stoichiometry on the Extensibility of Polyrotaxane Gels

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1. Materials

Polyethylene glycol (PEG) with M_n = 3.2×10^4 and M_w = 3.5×10^4 was kindly provided from Advanced Softmaterials Inc. A crude **PR-25** that consists of *α*–cyclodextrin (*α*–CD) and the same PEG was purchased from the same company. The molecular weight was determined by size-exclusion chromatography (SEC) with a calibration curve obtained by using polyethylene glycol (PEG) standards purchased from Polymer Source Inc. *α*–CD was purchased from Nihon Shokuhin Kako Co. Ltd. (CD content > 98.5%). 2,2-dimethylsuccinic anhydride was purchased from Tokyo Chemical Industry Co., Ltd. All other chemicals, including 1,1'-carbonyldiimidazole (CDI) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), were purchased from Wako Pure Chemical Industries, Ltd. All reagents were used without further purification, except for **PR-25**.

2. Measurements for characterization

^{1}H NMR spectra at 400 MHz were recorded on a JEOL JNM-AL400 spectrometer at 298 K and 353 K. Chemical shifts were calibrated using DMSO (2.50 ppm) as an internal standard. SEC with DMSO/LiBr as the eluent was performed on a Shodex OH Pack SB-G and two Shodex OHpac SB-806MHQ columns at 323 K with 1.0 mLmin^{-1}, using refractive index detection and PEG standards. The LiBr concentration was 10 mM.

3. Synthesis and purification of polyrotaxanes

PR-05 was synthesized by the following procedure. PEG (10.0 g) was dissolved in anhydrous pyridine (50 mL), and then DBU (86 μL, 0.57 mmol) and 2,2-dimethylsuccinic anhydride (1.94 mL, 17 mmol) were added. The solution was stirred at 55 °C overnight. The reaction solution was dropped into deionized water (300 mL), and then the pH was adjusted to 3.3 by using hydrochloric acid. The product was extracted with dichloromethane and then dried to obtain PEG-S (9.79 g) as a white solid. PEG-S (1.50 g) was dissolved in deionized water (6.0 mL), and then the aqueous solution of *α*–CD (6.00 g/44 mL) was added. The mixed solution was stirred for several minutes and then stood in a refrigerator at 5 °C for more than two days to obtain a turbid solution with white precipitate. It was confirmed that the longer complexation time did not affect the coverage and yield. It was suspended and freeze-dried to obtain a white powder that contains pseudo-polyrotaxane. The end-capping reaction is essentially the same as the conventional method that produces **PR-05**, except for the solvent. A solution of 1-adamantaneamine (65 mg, 0.43 mmol), BOP regent (190 mg, 0.43 mmol) and *N*-ethyldiisopropylamine (74 μL, 0.43 mmol) in anhydrous acetonitrile (75 mL) was mixed with the powder of pseudo-polyrotaxane under argon atmosphere. The suspension was stirred at room temperature for 48 hours. The resultant suspension was

centrifuged to remove the supernatant. The obtained solid was washed with acetonitrile twice, and then the solid was dried under vacuum. The obtained white solid was dissolved in DMSO (30 mL), and the solution was dropped into deionized water (300 mL). This aqueous solution was dialyzed by a membrane with MWCO = 14000. The dialyzed solution was then ultrafiltrated by a membrane with MWCO = 10000. Finally, the resultant solution was freeze-dried to obtain PR-05 (1.68 g) as a white solid.

Crude **PR-25** was purified by the following method, because it contains considerable amount of unthreaded *α*–CD and free PEG. The crude polyrotaxane (4.00 g) was dissolved in DMSO (40 mL), and the solution was dropped into deionized water. Obtained suspension was centrifuged to remove the supernatant, and the obtained precipitate was dried under vacuum. Then, the obtained solid was again dissolved in DMSO and then dropped into deionized water to generate the precipitate. The obtained precipitate was centrifuged and washed with deionized water twice. Finally, the washed solid was freeze-dried to obtain refined PR-25 (3.02 g) as a white solid.

4. Definition and calculation for the coverage of polyrotaxane

The coverage is a measure of how densely packed with CDs a main chain polymer is. The close packing corresponds to a coverage of 100%. For polyrotaxanes that consist of PEG and *α*–CD, The close packing has been defined by a molecular model study in which the CD:repeating unit ratio is 1:2.[1] The molar ratios obtained by the ^{1}H NMR spectra for **PR-05** and **PR-25** were 1:8 and 1:36, respectively. Thus, the coverage of **PR-05** can be calculated to be 5.6%, and **PR-25** is 25%.

5. Preparation of polyrotaxane gels

Purified polyrotaxane (150 mg) was dissolved in anhydrous DMSO (1.0-*V* mL). 20w/v% of CDI solution in DMSO was also prepared in another bottle. Both solutions contain catalytic amount of DBU: 0.005% and 0.001% for **PR-05** and **PR-25** gels, respectively. The CDI solution (*V* mL) was added to the solution of polyrotaxane to obtain pre-gel solution. The volumes of the added CDI solution were 25–125 μl, corresponding to 0.5–2.5w/v% of CDI in the pre-gel solutions. These pre-gel solutions were cross-linked at 60 °C overnight in a thickness-controlled mould. The mould consisted of a cut flat Teflon sheet with a thickness of 1.0 mm sandwiched tightly between glass slides. The void space created by the Teflon cut-out in the centre of the mould was 45 × 20 × 1.0 mm^3, and gelation of the pre-gel solutions was conducted in this space. The obtained gels were removed from the mould, and the edges were cut off to obtain rectangular gels for the tensile measurements. The size of gels was 40 × 3 mm.

6. Tensile measurements

The uniaxial tensile measurements were conducted by RSAIII (TA Instruments) at room temperature. The gels were stretched at a constant strain rate of 1%/s, which was sufficiently slow to exclude the time effect. For the accurate measurements, the initial gap between crossheads was adjusted to be 20–25 mm, though the maximum strain was limited to λ = 6–7 because of the limitation of the machine. Within the strain range, the absence of slip from the fixture was confirmed by the marking drawn on the surface of the gels. Since PR-05 gels were not fractured until λ = 6–7, the initial gap was changed to be 12 mm only for a PR-05 gel (CDI: 0.7%) to measure the behavior at higher strain, though the accuracy becomes lower. Although there was no slip at λ < 6, non-negligible slip from the fixture was observed at higher strain regime; the gap increased twelve-folds but the observed strain of the gel was about ten, indicating 20% of slippage at λ = 12. The less-accurate stress–strain data was shown in Figure S1a. Subsequently, the strain was held at λ = 12 to observe the stress relaxation, and the data was shown in Figure S1b.

7. Figure S1: A tensile data at higher strain and a stress relaxation data

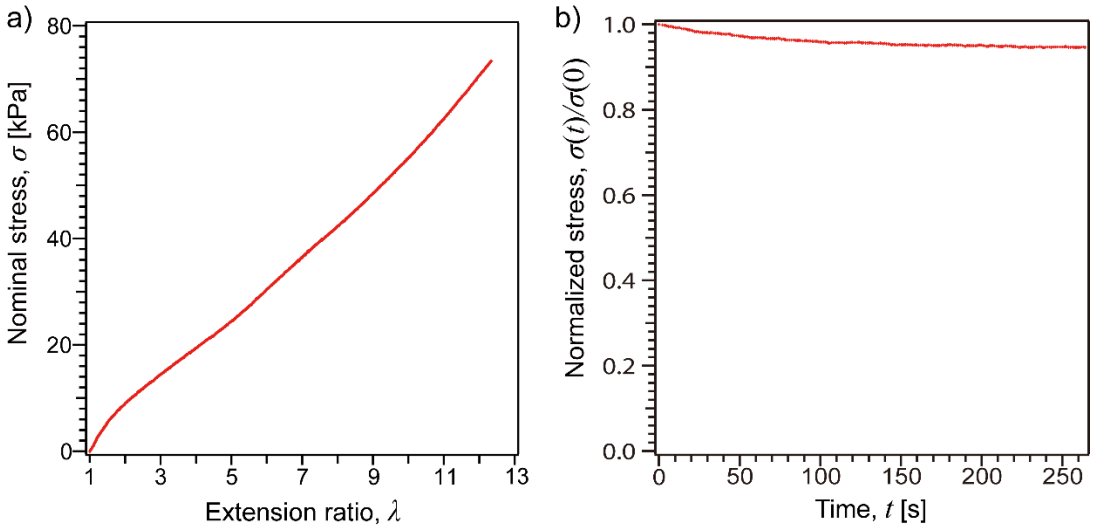

Figure S1. (a) Stress-strain curves for a PR-05 gel with 0.7% of CDI until λ = 12. Note that the accuracy of the data at λ > 6 gradually became lower with the increase of the strain because of the slip of gels from the fixture. The maximum slip was 20% at λ = 12, meaning that only about 10 times stretch in length was applied at λ = 12. (b) Stress relaxation after imposition of the uniaxial elongation of λ = 12. The time t = 0 corresponds to the state just after the strain imposition. The stress is reduced by the value at t = 0. Almost no stress relaxation (less than 5%) is observed.

[1] A. Harada, J. Li, M. Kamachi, *Macromolecules* **1993**, *26*, 5698–5703.