Supporting Information

Freestanding Tough Glassy Membranes Produced by Simple Solvent Casting of Polyrotaxane Derivatives

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1. Materials

A precursor polyrotaxane with 25% coverage (n-PR-25) consisting of polyethylene glycol (PEG; $M_{\rm n} = 32,000, M_{\rm w} = 35,000$) and α -cyclodextrin (α -CD) was kindly provided by Advanced Softmaterials, Inc. PEG with the same molecular weight was purchased from Fluka, and α -CD was purchased from Nihon Shokuhin Kako Co., Ltd. 2,2-Dimethylsuccinic anhydride and 4dimethylaminopyridine (DMAP) were purchased from Tokyo Chemical Industry Co., Ltd. All other chemicals and solvents were purchased from Wako Pure Chemical Industries, Ltd., and all the reagents were used without further purification.

2. Measurements for characterization

¹H NMR spectra were recorded at 400 MHz using a JEOL JNM-AL400 spectrometer at 353 K in deuterated dimethyl sulfoxide (DMSO- d_6). The chemical shifts were calibrated using tetramethylsilane (0 ppm) as an internal standard. Size-exclusion chromatography (SEC) with dimethylformamide (DMF)/lithium bromide (LiBr) as the eluent was performed using a Shodex OH Pack SB-G instrument with two Shodex OHpac SB-806MHQ columns at 323 K and 0.4 mL·min⁻¹, using refractive index detection. The LiBr concentration was 10 mM. Thermogravimetric analysis (TGA) was performed on a Rigaku Thermo Plus Evo instrument under N₂ at a heating rate of 10 K·min⁻¹. Powder X-ray diffraction (XRD) measurements were performed using an X-ray diffractometer (Rigaku SmartLab) with Cu K α radiation ($\lambda = 1.542$ Å).

3. Synthesis of native precursor polyrotaxanes (n-PRs)

All the different-coverage precursor polyrotaxanes (n-PRs) were synthesized from the same PEG and α -CD. n-PR with 7% (n-PR-07) was synthesized using a previously reported method.^[1] n-PRs

with 13% and 15% coverage (n-PR-13 and n-PR-15) were synthesized with only minor changes in the concentration of α -CD during the threading process. The detailed procedure is described below.

Dried PEG (10.0 g, 0.29 mmol) was dissolved in anhydrous pyridine (45.0 mL), and 1,8diazabicyclo[5.4.0]undec-7-ene (85.5 µL, 0.57 mmol) and 2,2-dimethylsuccinic anhydride (1.97 mL, 17 mmol) were added. The reaction solution was stirred at 55 °C overnight, after which it was cooled to 25 °C, acidified with hydrochloric acid (pH = 3.1), and extracted with dichloromethane. The solvent was evaporated and dried under vacuum to obtain demethylated PEG (PEG-S) as a white solid (9.9 g). The degree of modification was determined to be 95% by ¹H NMR spectroscopy. The PEG-S (8.98 g, 0.28 mmol) was dissolved at 70 °C in deionized water (45 mL) and a hot aqueous solution of α-CD (72 g in 255 mL) at 70 °C was added. The mixed solution was stirred for 5 min and then incubated at 35 °C for 3 d. The resultant turbid solution was freeze-dried to obtain a pseudopolyrotaxane, which is an inclusion complex of PEG-dS and α -CD, as a white solid. 1-Aminoadamantane (396 mg, 2.62 mmol), (benzotriazol-1-yloxy)tris(dimethylamino)phosphonium hexafluorophosphate (BOP reagent) (1.16 g, 2.62 mmol), and N,N-diisopropylethylamine (447 µL, 2.62 mmol) was dispersed in anhydrous DMF (300 mL) and the slightly turbid solution was added to the previously prepared pseudo-polyrotaxane. The mixture was stirred at room temperature (~25 °C) for 3 d. The resultant suspension was centrifuged, and the precipitate was washed three times with acetonitrile. The washed precipitate was dissolved in DMSO (100 mL), and the solution was poured into deionized water (600 mL). The resultant solution was dialyzed using a membrane with a molecular weight cut-off (MWCO) of 14,000, after which it was ultrafiltered through a membrane with MWCO = 10,000. Finally, the solution was freeze-dried to obtain 9.71 g of a polyrotaxane with 13% coverage (n-PR-13) as a white solid. Another polyrotaxane with 15% coverage (n-PR-15) was synthesized using the same procedure, indicating that the coverage can be varied in this range. The coverage, reflecting the packing density of CDs on the main-chain polymer, was defined as follows: The close packing that corresponds to a coverage of 100% is the state where the CD:PEG-repeating unit ratio is 1:2, which was also supported by a molecular model study.^[2]

Figure S1a shows the ¹H NMR spectra of the three different-coverage n-PRs. All peaks were successfully assigned as shown, and the molar ratio between α -CD and the repeating unit of PEG

were obtained from the integration ratio to obtain the coverages. The molar ratio between the monomer units of PEG and α -CD was obtained from the integral values at 4.8 ppm (corresponding to C1H of α -CD) and 3.7–3.2 ppm (other CH of α -CD and PEG). When the ratio of integral values at 4.8 ppm and 3.7–3.2 ppmis 1:*x*, the net integral value of PEG is x - 6. Thus, each α -CD, which has six-membered ring, has 6(x - 6) protons of PEG. Because each monomer unit has four protons, it corresponds to 6(x - 6)/4 monomer unit of PEG. When the monomer unit is two for each CD, it is defined as the dense packing. Therefore, the coverage, ϕ_{CD} , is calculated as

$$\phi_{\rm CD} = \frac{2}{\frac{6(x-6)}{4}} = \frac{4}{3(x-6)}$$
 (S1)

 ϕ_{CD} were calculated to be 13%, 15%, and 25% for n-PR-13, n-PR-15, and n-PR-25 respectively. **Figure S1b** shows the SEC traces of n-PR-15 and n-PR-13. Each polyrotaxane exhibited a single peak corresponding to an apparent molecular weight larger than that of PEG or α -CD. This indicates that the PEG and α -CD detected by NMR had formed a complex, that is, a polyrotaxane, rather than a simple mixture.



Figure S1. (a) ¹H NMR spectra (400 MHz, DMSO- d_6 , 353 K) and (b) SEC traces (detector: RI, eluent: DMF/LiBr) of n-PRs. The SEC trace of n-PR-25 is not shown because it is not soluble in the eluent and another trace with DMSO/LiBr eluent was previously reported.^[3]

4. Derivatization of polyrotaxanes

Propionylation of the hydroxyl groups of the CDs threaded in each n-PR was performed as follows. For n-PR-15 and n-PR-13, each polyrotaxane (4.0 g) was dissolved in anhydrous DMF (80 mL) before pyridine (12 mL) was dried and DMAP (384 mg, 3.14 mmol) was added. Propionic anhydride (25 mL, 153 mmol) was added dropwise to the solution, and the mixed solution was stirred overnight at room temperature. The reaction solution was poured into deionized water (1 L) to precipitate the hydrophobic product. The obtained suspension was centrifuged to collect the precipitate. The precipitate was washed with deionized water and collected by centrifugation. This washing process was repeated once more. Finally, the washed precipitate was freeze-dried to obtain each thermoplastic hydrophobic propionylated polyrotaxane. The weights of the isolated propionylated polyrotaxane with 15% coverage, **PR-15**, and that with 13% coverage, **PR-13**, were 5.43 g and 5.70 g, respectively.

For n-PR-25, because it is not soluble in pure DMF, lithium chloride (37.5 g, 885 mmol) was added to 500 mL of anhydrous DMF. n-PR-25 (46.5 g) was dissolved in the solvent, and then dried pyridine (180 mL, 2.23 mol), DMAP (5.00 g, 40.9 mmol), and propionic anhydride (280 mL, 2.19 mol) were added dropwise dropped into the solution. The same reaction and purification processes mentioned above were performed. Finally, 65.4 g of a propionylated polyrotaxane with 25% coverage, **PR-25**, was obtained. The degree of substitution was roughly estimated based on the integration ratio between the anomeric proton (C1H) at 5.1–4.8 ppm and the methyl signal at 1.1–0.9 ppm.

5. Membrane preparation

Freestanding membranes of 10-20 µm thickness were prepared from concentrated solutions of each polyrotaxane derivative, and thinner freestanding membranes of ~1 µm thickness were prepared from diluted solutions of PR-25. Thicker membranes were prepared as follows: PR-25 (2.00 g) was dissolved in 6.00 mL (473 mg) of acetone. The 30 wt% solution was filtered through a polytetrafluoroethylene (PTFE) membrane with a pore size of 0.45 µm, and then the filtrate was degassed in an ultrasonic bath for 30 s. The solution (0.6 mL) was cast on a polyethylene terephthalate (PET) film, whose surface was coated with silicone, and then immediately coated with an applicator. The gap of the applicator was 100 μ m, and the crosshead speed was 10 mm s⁻¹. After drying, the membrane and base film were cut into a circle with a 60 mm diameter, and then the membrane was peeled off from the base film for further measurements. The thickness of the membranes was $14.5 \pm$ 0.5 μ m based on four separately prepared films (N= 4). Some photographs taken during this process are shown in Figure 2a in the main text. PR-15 and PR-13 membranes were prepared by the same process, except that the concentration of the acetone solutions was higher: 0.81 g of the polyrotaxane was dissolved in 1.6 mL of acetone to obtain a 39 wt% solution. The thicknesses of the membranes were $18.0 \pm 2.2 \,\mu\text{m}$ (N= 3) and $18.5 \pm 1.7 \,\mu\text{m}$ (N= 4) for **PR-15** and **PR-13**, respectively.

Thinner freestanding membranes were prepared from diluted solutions of **PR-25** using the same procedure mentioned above. An 11 or 13 wt% acetone solution was cast and then coated with an applicator with a gap 30 μ m of. The dried membranes were peeled off from the base film, as shown in Figure 2c. The thicknesses of the membranes prepared from the 11 and 13 wt% samples were approximately 850 ± 100 nm and 1050 ± 100 nm, respectively, as measured using an optical interferometer (F54-XY-200-UV, Filmetrics).

6. Bulge test for membranes

Measurements were performed with the previously set-up bulge chamber.^[4,5] Polyrotaxane membranes with 13–17 μ m thicknesses were fixed over the hole of 3 mm in diameter, and then pressure was applied by dry N₂ gas. A schematic of the chamber and the parameters is shown in **Figure S2**. The film height was measured using a surface scanning laser confocal displacement meter (LT-9100M, KEYENCE, Co.) and direct observation from the lateral direction through a polished quartz sample holder. The applied pressure was controlled by a digital mass flow controller (F-201CV-100-RAS-11-V, Bronkhorst High) and a digital pressure controller (P–702CV-21KR-RAD-11-V, Bronkhorst High). Stress–strain curves were obtained from the relation between the applied pressure, *p*, and actual film height (bulge height), *h*, using the following equations:

Stress:
$$\sigma = \frac{PR}{2t} = \frac{2(a^2 + h^2)}{4th}$$
 (S2)
Strain: $\varepsilon = \frac{s - s_0}{s_0}$ (S3)
 $s = \theta R = \tan^{-1} \left(\frac{h}{a}\right) \frac{2(a^2 + h^2)}{h}$ (S4)

where *s* is the arc length, s_0 is the initial arc length, *t* is the sample thickness, *a* is the film radius, and θ and *R* are the angle and bulge radius of curvature, respectively.



Figure S2. Parameters for the bulge tests.

A video of the bulge test for a **PR-25** membrane is also available. The MP4 file named "video of bulge test" is a $64\times$ -speed video filmed in the lateral direction through the polished quartz sample holder from the beginning of the test to the bursting of the membrane.

Although the stress data from the thin films are less reliable owing to the inaccurate thicknesses for thinner membranes, the same bulge tests were also performed for thinner membranes of **PR-25**. Freestanding membranes with thicknesses of 850 nm and 1050 nm were measured in the same way as that used for the thicker membranes to obtain the stress–strain relationships shown in **Figure S3**. The Young's modulus, *E*, was approximately 1 GPa, and the yielding stress, σ_y , was approximately 25 MPa, similar to those of the thicker membranes and the melt-press-molded bulk films.



Figure S3. Stress–strain curves obtained by the bulge test of thin **PR-25** membranes with (a) 1050 nm and (b) 850 nm thicknesses.

7. Uniaxial tensile test for bulk films

Bulk films (0.2 mm in thickness) were prepared by melt-press molding of the propionylated polyrotaxane powder. The obtained films were cut into dumbbell-shaped specimens for measurements. Uniaxial tensile measurements were conducted using an AGS-1kNX STD (Shimadzu) instrument at room temperature. The specimens were stretched at a constant strain rate of 0.5 min⁻¹,

which is sufficiently slow to exclude the time effect. The obtained stress–strain relationships for bulk films with different coverages are shown in **Figure S4**.



Figure S4. Stress–strain curves of the melt-press-molded bulk films of propionylated polyrotaxanes with different coverages. Inset: Magnification at small strains (≤ 0.5).

8. Recyclability test

The recyclability of the polyrotaxane membranes was confirmed by the repeatability of the solvent process and the reproducibility of the mechanical properties as follows: Three membranes of PR-25 with thicknesses of $14.5 \pm 0.5 \,\mu\text{m}$ were prepared and cut into a total of 52 dumbbell-shaped specimens. All the virgin samples were uniaxially stretched at a constant strain rate of 0.5 min⁻¹ until fracture, and then all fractured dumbbells were collected to prepare the recycled membranes. Fractured dumbbells (112 mg) were dissolved in 400 μ L of acetone, and the same solvent-casting process as that for the virgin sample was performed to obtain a sheet of recycled membrane with a thickness of 15 μ m. Ten dumbbells were obtained from this recycled membrane, and the same uniaxial tensile test was performed on all the recycled dumbbells. **Figure S5** shows the scheme of the experiments and all the stress–strain curves of the virgin and recycled samples. The Young's modulus was almost the

same as that of the virgin samples, and the recycled samples were ductile with accompanying yielding. The yield stress of the recycled samples was 31 ± 0.5 MPa, which was similar to that of the virgin sample (32 ± 3.8 MPa). Although the stiffness and ductility were maintained in the recycled samples, the extensibility after the yielding point was considerably suppressed. This is probably due to the non-negligible damage to the polyrotaxanes induced by the large deformation.



Figure S5. Preparation scheme of the recycled membranes and stress–strain curves of the virgin and recycled samples.

9. Cross-sectional observation of membranes

The absence of pinhole in the membranes indicated by the success of the bulge tests was also confirmed by a confocal laser scanning microscopy. The cross-sectional profiles of the three membranes with different coverages were obtained by Confocal Microscope HYBRID C3 (Lasertec Corporation) and shown in **Figure S6**. All membranes have relatively smooth surface, except for PR-25 membrane, which has some dents on the surface probably because of the bubbles in the coated

solutions. However, the depth of the dents was considerably shallower than the thickness of the membranes, and no pinhole was observed.



Figure S6. Cross-sectional profiles of the membranes of (a) PR-25, (b) PR-15, and (c) PR-13. The coated membranes on PET were directly observed for PR-15 and PR-13, whereas the membrane of PR-25 was peeled off and then placed on a glass slide. The common steps on their right edges correspond to the cut edge of the membranes.

10. Viscoelastic measurements and master curves creation

The above-mentioned bulk films were also cut into rectangular shapes (typically $25 \times 3 \times 0.25$ mm) for viscoelastic measurements. Each obtained film was measured using a strain-controlled oscillatory rheometer (RSA-G2, TA Instruments). Temperature sweeps were conducted at 1-Hz oscillatory tensile strain to 0.05% strain. Frequency sweeps were conducted from 70 to 0.04 Hz, applying 0.05–0.10% of the oscillatory tensile strain amplitude. The time-temperature superposition was applied using a program in TRIOS (TA Instruments) for the data at different temperatures to obtain a master curve without vertical shifts. The master curve obtained at 25 °C for **PR-25** is shown in

Figure S7. Similar to the temperature sweep shown in Figure 5 in the main text, three relaxations were found in the master curve. It is notable that the timescale of the β -relaxation appears on a timescale of several microseconds, because the peak of tan δ is approximately 10⁶ Hz, which is much slower than the reported key motions that facilitate gas diffusion (these have a timescale of several tens of picoseconds).



Figure S7. A master curve of frequency-dependent moduli and tan δ for **PR-25** with the reference temperature at 25 °C. Peaks of tan δ of the main (α -) relaxation and two secondary relaxations (β and γ) are indicated by arrows.

11. Gas permeation test

The gas permeation properties were measured using differential pressure methods (ISO15105-1) under dry conditions with a differential pressure of 1 atm. For N₂ and CO₂ gases, measurements were performed with a K-315N-01 apparatus (Toyo-Rika Corporation) at room temperature (approximately 25 °C), and another instrument (GTR-1ADF-E, GTR Tec Corporation) was used for H₂ at 30 °C. Four different **PR-25** membranes of $14.5 \pm 0.5 \mu m$ in thickness, three **PR-15** membranes of $18.0 \pm 2.2 \mu m$ in thickness, and four **PR-13** membranes of $18.5 \pm 1.7 \mu m$ in thickness were measured. **Figure S8** shows the permeation curves obtained using dry N₂ and CO₂ gases. Because the permeability coefficient, *P*, is proportional to the slope at steady state, we can see that CO₂ is much

more permeable than N_2 in each membrane and that the permeability increases with decreasing coverage. The diffusion coefficient, *D*, was obtained from the delay time, θ ; the solubility coefficient, *S*, was obtained as *PID*, based on the assumption that the applied pressure is small enough to follow Henry's law. The averaged values of *P*, *D*, and *S* obtained from multiple measurements are shown in **Table 1** in the main text.



Figure S8. Time-course permeate pressures of CO_2 or N_2 through polyrotaxane membranes (\emptyset : 50 mm, thickness: 14–20 μ m) at 25 °C under 1 atm differential pressure.

12. Reference data of free volume size in a glassy polyrotaxane

In general, the diffusivity in a glassy polymer membrane is also significantly affected by the free volume, and robust high-free-volume polymers show very high CO₂ permeability without sacrificing selectivity.^[6,7] Although the free volumes were not measured for the three polyrotaxane membranes in this work, the comparison between another glassy polyrotaxane (H-PR-25), described in the main text as a previously reported hygroscopic polyrotaxane, and a conventional glassy polymer (polycarbonate: PC) may be helpful for understanding the general structure of polyrotaxanes. Each sample was prepared by melt-press molding, and the free volume radius, R_f , was obtained by positron annihilation lifetime measurement in the same way as described in our previous report.^[8] The R_f in H-PR-25 was determined to 0.27 nm, which was considerably smaller than that in PC (0.30 nm). The

relatively small free volume is attributable to the close packing of the bulky ring components, which occupy >80 wt% of the material; this is a common characteristic of glassy polyrotaxanes, including the polyrotaxane membranes in this work. Indeed, such close packing and homogeneous distribution of ring components were also observed in the reported polyrotaxane membranes, as suggested by the strong non-crystalline XRD peak near $2\theta = 7^{\circ}$ (Figure 3b), which shows the distance correlation between the rings.

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