Supplementary Information

Effect of Ring Size on the Mechanical Relaxation Dynamics of Polyrotaxane Gels

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Synthesis and purification of polyrotaxanes. A polyrotaxane (γ-PR) that consists of PEG and γ-CD was synthesized as follows. Aqueous solutions of PEG-NP (1033 mg / 10 mL) and γ-CD (17.89 g / 100 mL) were mixed and then left at room temperature overnight. Obtained dispersion was freeze-dried to yield crude pseudo-polyrotaxane as a white powder. A solution of *N*-ethyldiisopropylamine dissolved in anhydrous acetonitrile (0.50 mL / 84 mL) was added to the pseudo-polyrotaxane and then stirred at room temperature for 4 days to obtain a yellow dispersion. The dispersion was centrifuged and the supernatant was removed, then 50 mL of DMSO was added to the precipitate. After removing a small amount of the insoluble part by centrifugation, the solution was dropped into 700 mL of deionized water to precipitate the product. The obtained precipitate was

washed with deionized water three times. The same process of precipitation in water was performed again, and the obtained precipitate was freeze-dried to obtain γ-PR (1.70 g) as a white powder. On the other hand, purchased crude α-PR was purified by repeated precipitation in deionized water, because it contained a measurable amount of free α-CD that was not a polyrotaxane component. These two polyrotaxanes were used for the preparation of their cross-linked gels.

Preparation of polyrotaxane gels. Two series of polyrotaxane gels, α-PR and γ-PR gels, were prepared from solutions of α-PR and γ-PR, respectively, in DMSO by the following common procedure. The polyrotaxane, α-PR or γ-PR (281 mg), was dissolved in anhydrous DMSO (1.70 mL), and a solution of the cross-linker, hexamethylene diisocyanate, in DMSO (170 μL) with a catalytic amount of dibutyltin dilaurate (0.05 vol%) was added to obtain the pre-gel solution. The pre-gel solutions were prepared with different cross-linker concentrations. These solutions were cross-linked at 60°C for 17 h in a thickness-controlled mold. The mold consisted of a flat, cut Teflon sheet with a thickness of 3.0 mm sandwiched tightly between glass slides. The void spaces created by the Teflon cutouts in the center of the mold were $23 \times 23 \times 3.0$ mm^3, and gelation of the pre-gel solutions was conducted in these spaces. The obtained gels were removed from the molds, and the edges were trimmed. The gels were first immersed in DMSO containing 10% water and then placed in an oven at 40°C overnight to quench the reaction. The gels were then transferred to fresh DMSO, and the solvent was exchanged frequently to remove impurities. After three days of washing, the gels were stored in DMSO at room temperature until measurement. The treated gels were cylindrical with diameters of 21 ± 1 mm and thicknesses of 3.3 ± 0.3 mm. In each series of gels, five samples with different cross-linker concentrations were prepared: 0.75, 1.00, 1.25, 1.50, and 2.00 vol% for α-PR gels and 1.50, 1.75, 2.00, 2.25, and 2.50 vol% for γ-PR gels. The obtained α-PR and γ-PR gels were designated α-PR-g1 to g5 and γ-PR-g1 to g5, respectively. More cross-linkers were required for γ-PRs to obtain gels with similar elastic moduli to α-PR gels; it may be caused by the lower mol concentration of γ-PR pre-gel solutions.

Calculation of polyrotaxane coverages. The polyrotaxane coverage is a measure of how densely covered a backbone polymer is by ring components. For PEG, a polyrotaxane whose backbone is

completely covered with α-CDs has been defined by a molecular model study in which the α-CD:repeat unit ratio is 1:2. The same definition is applicable for single-stranded polyrotaxanes with γ-CDs, because the ring size does not affect the length of the backbone in the axial direction. From the ^{1}H NMR spectrum of γ-PR, the molar ratio of γ-CD and the PEG repeat unit was 1:7.2. Thus, based on the above-mentioned definition of coverage, the ratio corresponds to a 28% coverage. Since the molar ratio of α-CD and the PEG repeat unit was the same, the coverage of α-PR is also calculated to be 28%. To be exact, the surface coverage of γ-PR would be slightly smaller than the estimated value, because two of the CDs act as stoppers rather than as cyclic component threads, but the effect accounts for less than 1%.

Assignment of the plateaus obtained by dynamic viscoelastic measurements. When we assume that the higher plateau modulus E_∞ corresponds to the rubbery state, Eq. 3 calculates M_x to be 4000–8000, as shown in Table 2, which corresponds to a value of 3–6 for n_{CD}, which is the average number of CDs between cross-links. Since each polyrotaxane has 65 CDs on average, a single polyrotaxane provides 11–22 cross-links. On the other hand, if we assume instead that the lower plateau corresponds to the rubbery state, the modulus $E_\infty - \Delta E$ calculates M_x to be *ca*. 100000. This M_x is similar or slightly larger than the molecular weights of the precursor polyrotaxanes, meaning that one or more polyrotaxane forms a single partial chain. In short, the values of M_x correspond to $n_{CD} \gtrsim 65$, meaning that each single polyrotaxane provides one or less cross-link. Under ideal cross-linking conditions, more than two cross-links are necessary to form an infinite polymer network. Therefore, by comparing these two different pictures of polymer networks, the most probable assignment is that the higher plateau corresponds to the rubbery state. This assignment enables the following molecular interpretation of the viscoelastic relaxation, as was the case in our previous study of polyrotaxane gels.[14,15] The higher plateau exhibits rubber elasticity because the slidable cross-links behave as if they are fixed; the time scale for oscillatory deformation of the gels is much faster than that of chain sliding through the cross-links. The chains slide on the same time scale as relaxation, accompanying the relaxation of their orientation anisotropy, which is the origin of elasticity in the rubbery state. For the lower plateau, which has a longer time scale for

chain sliding, the orientation of chain segments became isotropic, and the arrangement entropy of the ring components would generate stress.
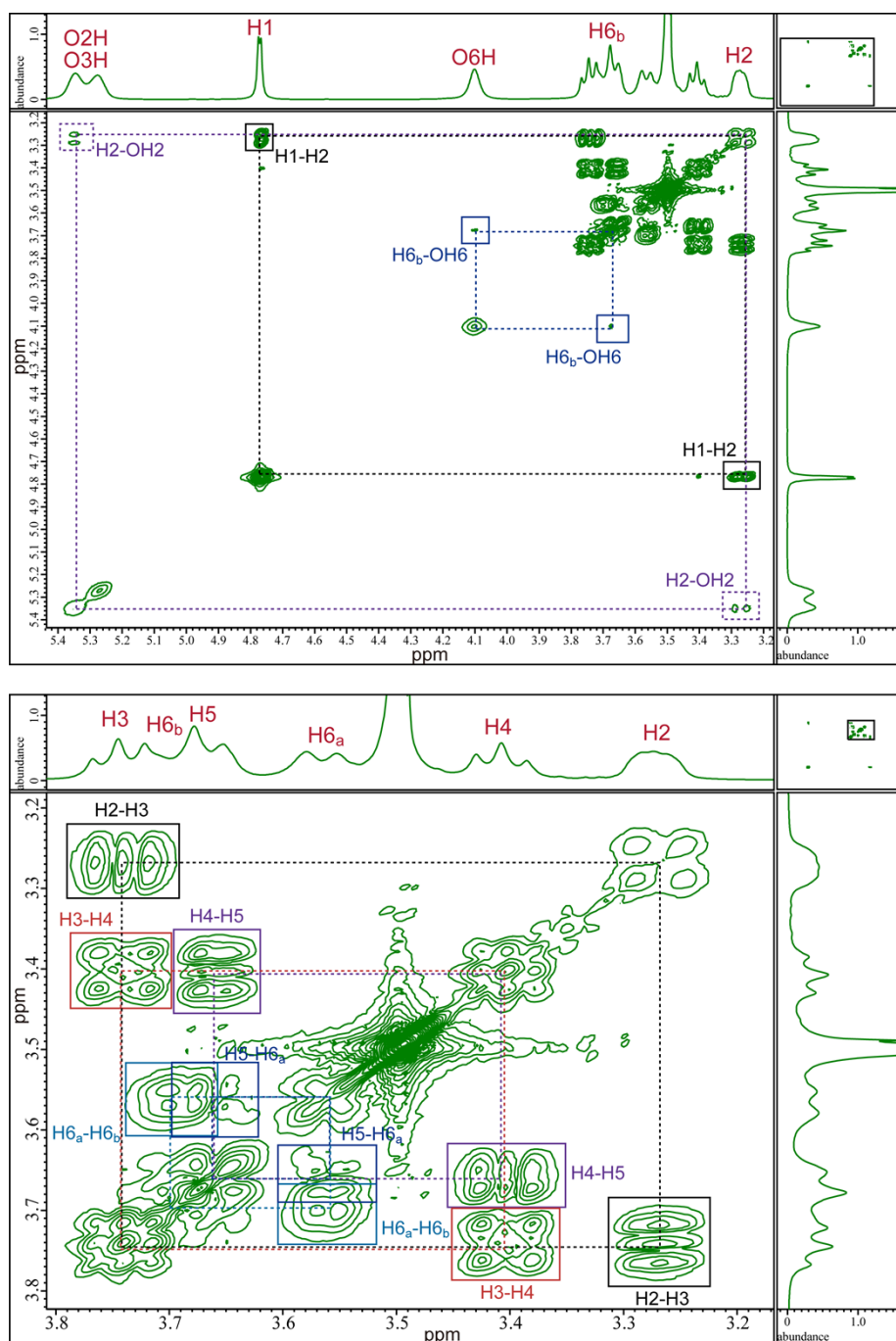
Figure S1. ^{1}H-^{1}H COSY NMR spectra of α-PR (400 MHz, DMSO-d_6, 343 K) and resonance assignments for the cyclodextrin protons. The full spectrum including the anomeric proton (top) and an expanded view of non-anomeric protons (bottom).
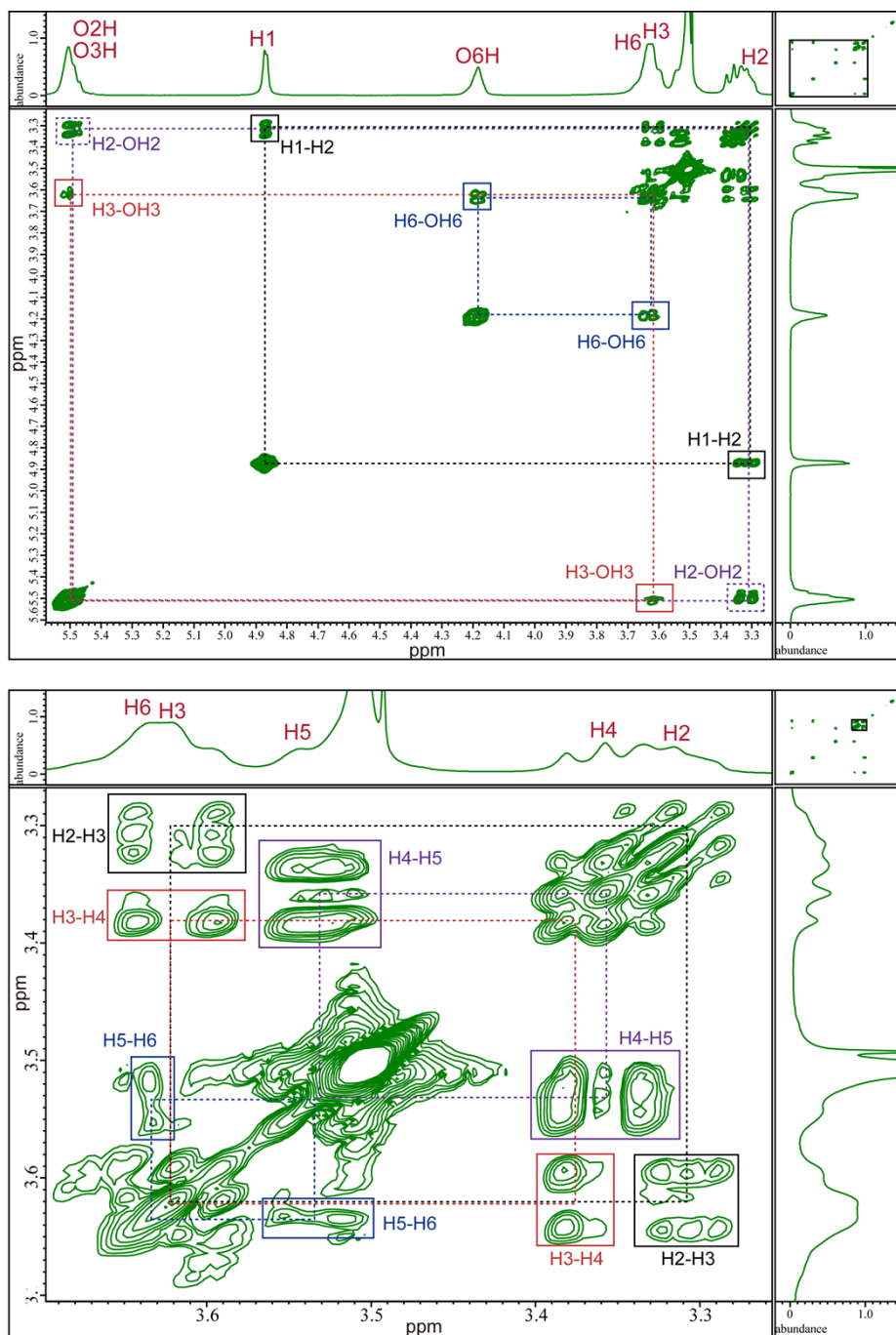
Figure S2. ^{1}H-^{1}H COSY NMR spectra of γ-PR (400 MHz, DMSO-d_6, 343 K) and resonance assignments for the cyclodextrin protons. The full spectrum including the anomeric proton (top) and an expanded view of non-anomeric protons (bottom).

Table S1. Fitting parameters and relaxation times τ_s of α- and γ-PR gels.

	E_∞ / kPa	ΔE / kPa	τ_{HN} / ms	α	β	τ_s / ms
α-PR -g1	103	95	679	0.798	0.536	344
-g2	170	160	177	0.774	0.522	85
-g3	150	138	353	0.918	0.450	172
-g4	223	212	86	0.857	0.738	64
-g5	270	261	85	0.766	0.656	53
γ-PR -g1	104	101	1570	0.755	0.742	1110
-g2	201	184	511	0.886	0.417	223
-g3	191	184	623	0.906	0.527	346
-g4	208	200	700	0.949	0.338	273
-g5	256	248	176	0.879	0.589	106