Supporting Information

Viscoelastic Properties of Slide-Ring Gels Reflecting Sliding Dynamics of Partial Chains and Entropy of Ring Components

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Calculation of mass content of CD of polyrotaxanes. Although the mass content of CD, w_{CD}, in the case of E-PR is easy to be calculated from the ^{1}H NMR spectrum as written in the main text, the situation is more complicated in B-PR. Because of a complication related to the unsaturation distribution of PBD, we employ the six-carbon unit of the main chain of PBD (except for vinyl carbon) rather than the monomer unit. With the exception of the vinyl group, the average molecular weight of the six-carbon unit of PB is 81. Since the ratio of 1,4- and 1,2-addition is 79:21, 0.13 vinyl groups will exist in every two-carbon unit on average, corresponding to 0.40 vinyl groups in a six-carbon unit. Therefore, the average molecular weight of a six-carbon unit was calculated to be 92. The ^{1}H NMR spectrum of B-PR in Figure 3b shows that the molar ratio between $\gamma-$CD and the six-carbon unit is 23:77. This corresponds to a weight ratio of 81:19, so the mass content of CD is $w_{CD} = 0.81$.

Calculation of surface coverage of polyrotaxanes. The surface coverage, SC, is a measure of how densely packed with CDs a main chain polymer is. For poly(1,4-butadiene), a polyrotaxane closely packed with CDs, corresponding to a coverage of 100%, has been defined by a molecular model study in which the $\gamma-$CD:monomer unit ratio is 2:3.[1] On the other hand, because of the unsaturation distribution of PBD in our case, we employ a synonymous definition in which a single $\gamma-$CD covers a six-carbon unit in the close-packed B-PR (Figure S1). Thus, from the molar ratio obtained by the ^{1}H NMR spectrum, the SC is estimated to be about 30%. In reality, the surface

coverage would be slightly smaller than the estimated value because two of the CDs act as the stopper rather than as cyclic component threads. For PEG, a polyrotaxane closely packed with α− CDs has been defined by a molecular model study in which the α− CD:monomer unit ratio is 1:2. Therefore, from the molar ratio obtained by the ^{1}H NMR spectrum, the SC is estimated to be 25%.

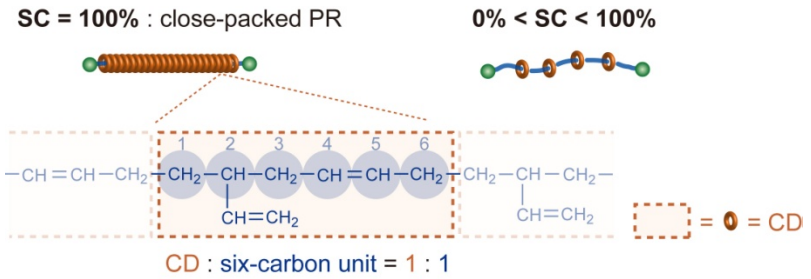

Figure S1. Definition of surface coverage (SC) of B-PR. SC is defined to be 100% when the γ− CD:six-carbon unit ratio is 1:1, indicating close-packed PR, in which the backbone polymer is fully covered with CDs. This definition is based on a molecular modelling study on a pseudo-PR consisting of CD and poly(1,4-butadiene)[1]. An SC of 0% represents not a PR but an end-capped polymer without a threaded CD.

Linear stress relaxation measurements of slide-ring gels. Compressive stress relaxation measurements were also conducted under similar conditions, except that a strain of 0.4% of the oscillatory compressive strain amplitude was applied only in the case of B-SR, which is still within the range of linear viscoelasticity. The relaxation modulus $E(t)$ of each gel is shown in Figure S2.

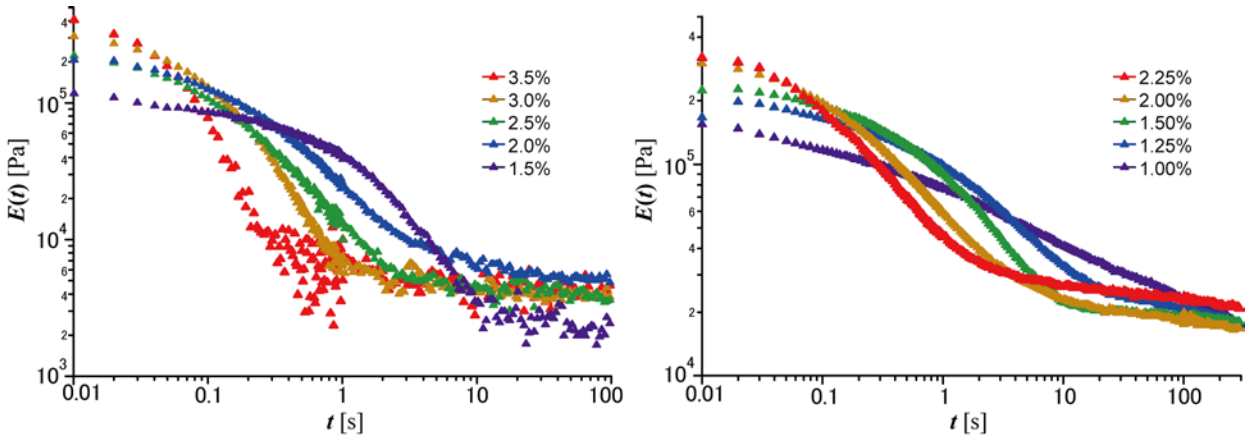

Figure S2. Stress relaxation moduli *E*(*t*) of slide-ring gels. $E(t)$ of the series of B-SR (left) and that of E-SR (right) with different cross-linker concentrations.

[1] T. Michishita, M. Okada, and A. Harada, *Macromol. Rapid Commun.*, 2001, **22**, 763.