Supplementary Information

Dynamic transition between rubber and sliding states attributed to slidable cross-links

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Contents

1.   Materials

Biscarboxyl-terminated polybutadiene (PB) was purchased from Aldrich; its M_n and M_w values were 3900 and 6220, respectively, as determined by size-exclusion chromatography (SEC) with a calibration curve obtained by using polyethylene glycol (PEG) standards purchased from Polymer Source Inc.   The unsaturation distribution was determined to be *trans*:*cis*:*vinyl* = 42:37:21 by comparing the ^{1}H NMR spectrum to the literature.[1]   *γ*-Cyclodextrin (CD) was purchased from Nihon Shokuhin Kako Co. Ltd. (CD content > 98.5%).   *N,N'*-Dicyclohexylcarbodiimide was purchased from Aldrich.   *p*-Nitrophenol was purchased from TCI.   Acetic anhydride was purchased from Kanto Chemical Co., Inc.   *N,N*-Diisopropylethylamine, all dehydrated solvents, and other chemicals were purchased from Wako Pure Chemical Industries, Ltd.   All reagents were used without further purification.

2.   Measurements for characterization

^{1}H NMR spectra at 400 MHz were recorded on a JEOL JNM-AL400 spectrometer at 298 K and 343 K. Chemical shifts were calibrated using DMSO (2.50 ppm) as an internal standard. Attenuated total reflectance-Fourier transform infrared spectra were recorded on a Nicolet 4700 instrument (Thermo Electron Co., Ltd.) equipped with a diamond attenuated total reflection accessory (DurasamplIR II, SensIR Technologies Technologies) in air.   Powdered samples were pressed onto a diamond window, and the obtained spectra were analysed with the spectrometer's OMNIC software.   SEC with DMSO/LiBr as the eluent was performed on two Shodex OHpac SB-G columns at 323 K, using refractive index detection and PEG standards.   The LiBr concentration was 10 mM.

## 3.   Synthesis and purification of polyrotaxane (PR)

A PR consisting of PB and CD was synthesized according to our previous report.[2]   The obtained product contains a by-product, as indicated by the SEC results (Figure S1), which show bimodal peaks corresponding to M_w = 260,000 (fraction 1) and 22,600 (fraction 2).   The two products were separated by SEC with DMSO/LiBr as an eluent, and then the two obtained solutions were dropped into de-ionized water to precipitate the products.   ^{1}H NMR spectra of these two products (Figure S2) revealed the surface coverage (SC) of PB with CD (see the following section regarding SC). The CD content is obviously much smaller in the product from fraction 1 than in that from fraction 2.   The product that showed a smaller M_w by SEC (fraction 2) has an SC of ca. 30%.   On the other hand, in the other product (fraction 1), each PB is accompanied by only about two CDs. This means that fraction 1 is an unavoidable by-product that was capped with two CDs at the ends

of a polymer without a threaded CD.   The large M_w value revealed by SEC may arise from an aggregation of the end-capped polymers.   The by-product is slightly soluble in DMSO (<2 wt%), whereas the refined PR is very soluble (>20 wt%).   Thus, the product of fraction 2 was collected as the refined PR by SEC.
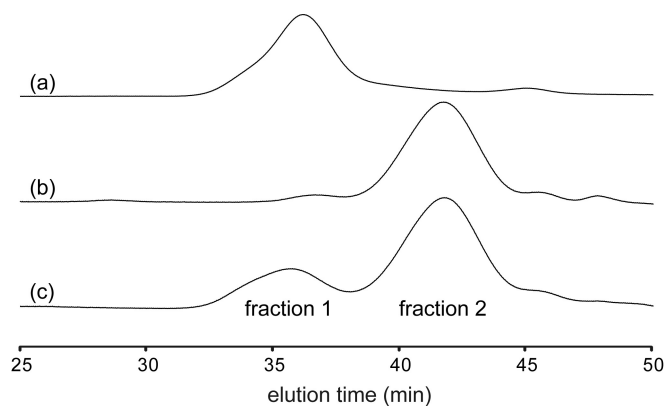
Figure S1.   Elution diagrams of PR before and after purification by SEC.
(a) Separated fraction 1 and (b) fraction 2 of (c) the SEC trace of crude PR. Fractions 1 and 2 are characterized as an unavoidable by-product and PR, respectively.   Detection: differential refractive index.
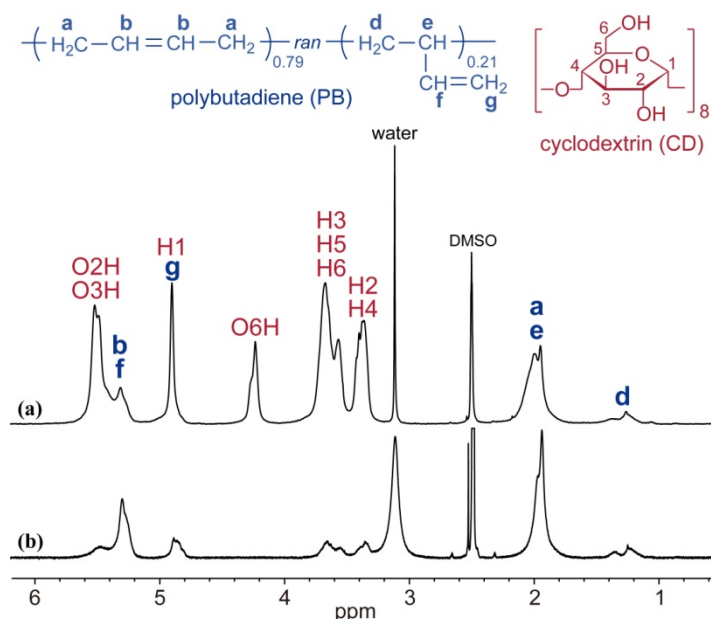

Figure S2.   Full spectra of ^{1}H NMR of refined PR and a by-product. (a) Refined PR collected as fraction 2 by SEC and (b) an unavoidable by-product consisting of end-capped PB without threaded CDs, collected as fraction 1. Measurements were made with DMSO-d_6 as the solvent at 343 K.   All signals were assigned as indicated: blue and red characters show the signals of PB and CD, respectively.

4.   Characterization of refined PR

Because of a complication related to the unsaturation distribution of PB, we employ the six-carbon unit of the main chain of PB (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 shows that the molar ratio between CD and the six-carbon unit is 1:3.39.   This corresponds to a weight ratio of 81:19, so the mass content of CD is $w_{CD} = 0.81$.

The SC is a measure of how densely packed with CDs a main chain polymer is.   For poly(1,4-butadiene), PR closely packed with CDs, corresponding to a coverage of 100%, has been defined by a molecular model study in which the CD:monomer unit ratio is 2:3.[3]   On the other hand, because of the unsaturation distribution of PB in our case, we employ a synonymous definition in which a single CD covers a six-carbon unit in the close-packed PR (Figure S3).   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.
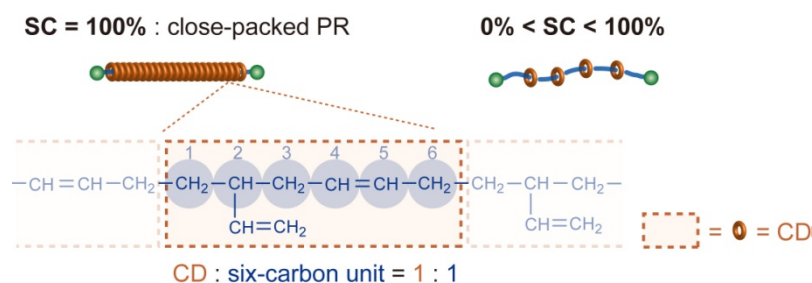
Figure S3.   Definition of surface coverage (SC) of PR.   SC is defined to be 100% when the CD:six-carbon unit ratio is 1:1, indicating close-packed PR, in which the backbone polymer is fully covered with CDs.   This definition is based on a molecular modelling study on a pseudo-PR consisting of CD and poly(1,4-butadiene)[3].   An SC of 0% represents not a PR but an end-capped polymer without a threaded CD.

The molecular weight of PR is roughly estimated from the SEC results using a PEG standard. The obtained values of M_w and M_n were 27,200 and 18,900, respectively.   These values are not far from the molecular weights calculated from the weight ratio obtained by ^{1}H NMR; ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ 5.9–5.6 (O2H, O3H), 5.5–5.2 (vinyl CH and vinylene), 4.9 (C1H of

γ-CD and vinyl CH_2), 4.5 (O6H), 3.7–3.4 (C3H, C5H, C6H), 3.4–3.2 (C2H, C4H), 3.3 (water), 2.1–1.8 (α-methylene and methine of alkene), 1.4-1.1 (β-methylene of alkene).   IR (cm^{-1}): 3342br, 2916s, 2843m, 1740w (carbonyl of ester), 1639m, 1435m, 1368m, 1155s, 1079s, 1027s, 967m (*trans* vinylene), 941m, 912w (vinyl), 860w, 759w, 704w.

5.   Preparation of slide-ring gels

The purified PR (23.0 mg) was dissolved in anhydrous DMSO (135 µl), and then the solution of cross-linker in DMSO (15 µl) with a catalytic amount of dibutyltin dilaurate was added to obtain the pre-gel solution.   The cross-linker was hexamethylene diisocyanate, and the catalyst concentration was 0.05 vol%.   Three different pre-gel solutions were prepared with cross-linker concentrations of 1.5, 2.5, and 3.5 vol%, respectively.   These solutions were cross-linked at 333 K for 18 hr 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 $12 \times 12 \times 1.0$ 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.   The gels were first immersed in DMSO containing 10% water and then left in an oven at 333 K overnight to quench the reaction.   They were then transferred to fresh DMSO and left in an oven at 333 K.   The solvent was exchanged frequently to remove impurities from the gels.   After a week of washing, the gels were stored in DMSO at room temperature until measurement.   The size of the gels did not change much throughout the above treatments; swelling and contraction induced a change in thickness of 3% or less. The treated rectangular gels, which are 9.4 ± 0.5 mm wide and 1.00 ± 0.03 mm thick, were used for the viscoelasticity measurements.

6.   Viscoelasticity measurements

The dynamic mechanical measurements were conducted with a strain-controlled oscillatory rheometer (RSAIII, TA Instruments) using a parallel plate geometry.   The lower plate was attached to a Petri dish filled with anhydrous DMSO.   All measurements were conducted in the solvent to keep the gels from drying.   Before the measurements, the gels were kept in the solvent at 303 K for at least 30 min to achieve equilibrium swelling, and then a small compression was loaded in advance with a stress of 3 mN.   Frequency sweeps were conducted from 0.01 to 80 Hz at 303 ± 1 K, applying 0.2% of the oscillatory compressive strain amplitude.

7.   Stress relaxation measurement

Compressive stress relaxation measurements were also conducted under similar conditions, except that a strain of 0.4% of the compressive strain was applied, which is still within the range of

linear viscoelasticity. The relaxation modulus $E(t)$ of each gel is shown in Figure S4. The relaxation time obviously decreased with increasing cross-linker concentration. The relaxation time τ_s can also be estimated from this relaxation data, although the accuracy decreases for faster relaxation. Thus, the τ_s value of the gel with a cross-linker concentration of 1.5% is estimated to be 0.9 s, as depicted in the figure. This value agrees well with the τ_s value (0.8 ± 0.3 s) obtained from the dynamic measurement (Figure 2) using equation (2).
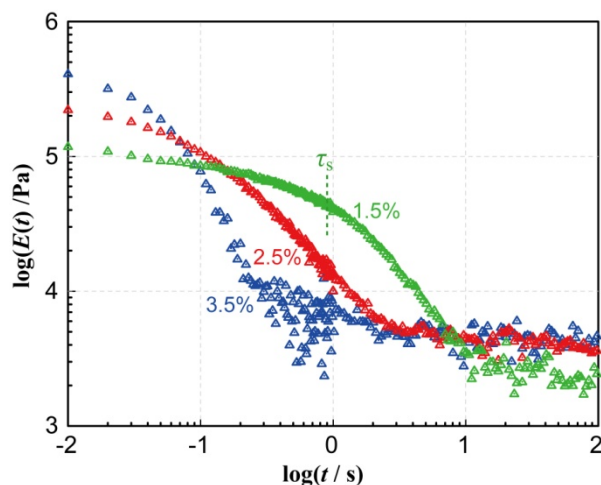
Figure S4. Stress relaxation moduli $E(t)$ of slide-ring gels. Numbers indicate the cross-linker concentration. Green dashed line indicates the relaxation time τ_s of the gel with 1.5% cross-linker obtained by stress relaxation measurement. Relaxation times of the other two gels are not shown because of the lower accuracy of their faster relaxation.

8. Measurement of the density of polymeric material in gels

First, the weight of the swollen gel at 303 K, w_{gel}, was measured. Then, the gel was immersed in de-ionized water to expel the solvent, and the resulting shrunken gel was dried completely under vacuum for several days so its dry weight w_{dry} could be measured. The density of polymeric material ρ [g/m^3] in each gel is given by $\rho = w_{dry}d/w_{gel}$, where d is the density of the gel. Since the density of the gel is similar to that of the solvent, we employed the value for DMSO ($d = 1.1 \times 10^6$ [g/m^3]) for the calculations.

References

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