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

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Supporting Information

ABSTRACT: A systematic study of the viscoelastic relaxation of slide-ring gels revealed the dynamics of chains sliding through the cross-links, based on a precise assignment of the plateau moduli and on detailed consideration of the correlation between relaxation times and the molecular weights between cross-links. The slide-ring gels exhibit finite equilibrium moduli that are much smaller than those of the rubbery plateau, indicating a significant contribution of the ring components’ entropy to the elasticity. Viscoelastic measurements were performed on two series of slide-ring gels with polybutadiene or poly(ethylene glycol) as the axis polymers. The elastic moduli at the rubbery plateaus and the measured densities of the elastic bodies allow derivation of the average molecular weights between the cross-links, Mx. The relaxation time in each gel series indicates a cubic power dependence on Mx. By analogy to polymer entanglement, the relaxation can be attributed to a reptation-like local diffusion of partial chains.

INTRODUCTION

Mechanically interlocked molecules such as rotaxane and catenane are characterized by intramolecular mobility. Each component of the molecule fluctuates independently within topological restrictions; in the case of rotaxane, the ring component rotates and slides on the axis.1 When the characteristic mobility of small molecules in solution is extended to macromolecules, various functional polymers can be designed, as represented by polyrotaxanes.2 The most common design is based on chemical modifications of the ring components with various functional molecules, so that the functions are integrated with the sliding of the rings along the polymer axes. For example, a polyrotaxane whose ring components were modified by maltose displayed enhanced binding to a sugar-binding protein because of the effective multivalent interactions supported by the slidable sugar moieties.3 Similarly, polyrotaxanes modified with cationic oligomers4 and mesogens5 were prepared for the purpose of effective gene delivery and as fast-response liquid crystals, respectively. The diversity of possible chemical modifications promises further advancement in molecular design based on the combination of molecular functionality and slidability characteristics.

The microscopic mobility is amplified at the macroscopic level by the unique cross-linking of polyrotaxanes. The coupling of ring components that belong to different polyrotaxanes yields a polymer network, the so-called slide-ring gel, in which each polymer chain is topologically connected via figure-eight cross-links (Figure 1).6 Thus, the chains are allowed to slide through the cross-links, and this local mobility affects the material properties through the network. Indeed, various abnormal behaviors of slide-ring gels have been observed, such as invariant inhomogeneity7 and isotropic orientation8 under deformation. These properties are rather peculiar in polymer liquids, whereas chemically cross-linked rubbers and gels exhibit enhanced inhomogeneity and anisotropic orienta-
The microscopic behaviors of slide-ring gels, similar to uncross-linked amorphous polymers, are interpretable generally by the microscopic sladdability of the polymer chains. That is, deformations of slide-ring materials do not induce the deformation of the polymer chains but, rather, induce the transfer of chains through the cross-links, resulting in isotropic orientation (Figure 2). This interpretation has also been applied for other peculiar properties, such as suppressed stretch-induced swelling and minimum strain coupling on biaxial deformation.

The slidability of chains is, however, still insufficient for explaining the mechanical characteristics of slide-ring gels. Specifically, how does the material remain elastic despite the isotropic orientation under deformation? Generally, the elasticity of rubbers and gels arises from the orientation anisotropy of the chain segments under deformation (see the left illustration in Figure 2). Thus, materials without anisotropy under deformation are liquids, such as polymer melts. It is unlikely that the original shape of the material will be restored by the isotropic chains (Figure 2, right) when the external stress is removed. In fact, it is obvious that a slide-ring gel is an elastic body, as evidenced by the stress−strain behavior without hysteresis. The concave upward stress−strain curve, which is entirely distinct from the concave downward one of chemically cross-linked materials, is suggestive of the significantly low elastic modulus. Empirically, slide-ring gels are rather softer than chemical gels under the same concentration of cross-linkers. It should be pointed out that such a comparison whether the slide-ring gels are significantly softer than the chemical gels.

A significant finding that provides new insight into both the origin of elasticity and the softness of slide-ring gels was revealed recently because of a synthetic breakthrough in polyrotaxanes. Until very recently, almost all slide-ring gels had been prepared from a single-species polyrotaxane that contained poly(ethylene glycol) (PEG) as the axis polymer. The reason for this was the well-designed and established synthesis for the polyrotaxane and the difficulty of changing the polyrotaxane axis. Indeed, studies on polyrotaxanes have also concentrated on those that are PEG-based, whereas pseudopolypolyrotaxanes, which are equivalent to polyrotaxanes without end-capping groups, have had a wide range of backbones. Recently, a versatile method for the synthesis of diverse polyrotaxanes was developed; three polyrotaxanes were synthesized from different backbone polymers and different cyclodextrins (CDs) by a single method. This synthetic breakthrough has enabled us to produce a new class of slide-ring gels with various non-PEG backbones. Finally, as we reported very recently, a peculiar viscoelastic relaxation that is attributable to the dynamics of sliding was observed in a series of polybutadiene (PBD)-based slide-ring gels, and this observation alerted us to the possible contribution of the cyclic components to the elasticity.

We report herein the viscoelastic properties of two different series of slide-ring gels, B-SR and E-SR, which were respectively prepared from the PBD-based (B-PR) and PEG-based (E-PR) polyrotaxanes. These precursor polyrotaxanes were purified and characterized, and the gels prepared from them were washed to remove unreacted starting materials before viscoelastic measurements. Systematic and careful measurements within the range of linear viscoelasticity, less than 1% strain, detected a relaxation in the E-SR that was similar to that in the B-SR. The viscoelastic results in each series of slide-ring gels were precisely analyzed to assign observed plateaus and to estimate the molecular weights between cross-links. Based on these assignments and the molecular-level information on the network, molecular pictures of the viscoelastic behaviors were discussed.

## EXPERIMENTAL SECTION

**Materials.** A crude polyrotaxane consisting of PEG and α-CD (E-PR) was purchased from Advanced Softmaterials Inc. The axis PEG had a number-average molecular weight, $M_n$, of 32 000 and a weight-average molecular weight, $M_w$, of 35 000. Bis-carboxyl-terminated polybutadiene (PBD) 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 using 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 literature values. γ-Cyclodextrin (γ-CD) was purchased from Nihon Shokuhin Kako Co. Ltd. (CD content >98.5%). N,N′-Diethyloxycarbodiimide (DCC) was purchased from Aldrich. p-Nitrophenol was purchased from TCI. N,N′-Disopropylethylamine, anhydrous solvents, and other chemicals were purchased from Wako Pure Chemical Industries, Ltd. All reagents were used without further purification.

**Measurements for Characterization.** 1H NMR spectra at 400 MHz were recorded on a JEOL JNM-AL400 spectrometer at 298 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 in air on a Nicolet 4700 instrument (Thermo Electron Co., Ltd.) equipped with a diamond attenuated total reflection accessory (DurasampIR II, SensIR Technologies). Powdered samples were pressed onto a diamond window, and the obtained spectra were analyzed with the spectrometer’s OMNIC software. SEC with DMSO/LiBr as the eluent was performed on two Shodex OHPak SB-G columns at 323 K, using refractive index detection and PEG standards. The LiBr concentration was 10 mM. SEC with chloroform as the eluent was performed on two Shodex GPC LF-840 columns at 313 K.

**Synthesis and Purification of Polyrotaxanes.** The polyrotaxane consisting of PBD and γ-CD (B-PR) was synthesized according to our previous report. The obtained product contained, as a byproduct, a PBD in which both ends were capped with γ-CD without a threaded γ-CD. As the result of aggregation, the byproduct exhibited a very large $M_n$ (ca. 260 000) by SEC chromatography with DMSO/LiBr as an eluent. The byproduct was eliminated by SEC, and the obtained B-PR solution was dripped into deionized water to precipitate the product. By freeze-drying the precipitate, refined B-PR was obtained as a white powder. Crude polyrotaxane consisting of PEG and α-CD (E-PR) was purified by repeated reprecipitation in deionized water because it contained a measurable amount of free α-CD that was not a polyrotaxane component. These refined polyrotaxanes were used for the preparation of slide-ring gels.
Preparation of Slide-Ring Gels. The slide-ring gels, B-SR and E-SR, were prepared respectively from solutions of B-PR and E-PR in DMSO by the following procedures. The refined B-PR (23.0 mg) was dissolved in anhydrous DMSO (135 μL), and a solution of cross-linker in DMSO (15 μL) with a catalytic amount of dibutyltin dilaurate (0.05 vol %) was added to obtain the pregel solution. The cross-linker was hexamethylene diisocyanate; pregel solutions were prepared with different cross-linker concentrations. These solutions were cross-linked at 60 °C for 18 h in a thickness-controlled mold. The mold for B-SR consisted of a flat, cut Teflon sheet with a thickness of 1.0 mm sandwiched tightly between glass slides. The void space created by the Teflon cutout in the center of the mold was 12 × 12 × 1.0 mm³, and gelation of the pregel solutions was conducted in these spaces. The refined E-PR was also cross-linked in a similar way, although on a larger scale; the void space was 27 × 25 × 3.0 mm³.

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 333 K overnight to quench the reaction. They were then transferred to fresh DMSO and placed 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 significantly during the preceding treatments; swelling and contraction induced changes in thickness of 120% or less. The treated gels of B-SR were square with 9.4 ± 0.30 mm thickness, and the gels of E-SR were cylindrical with a diameter of 20.0 ± 1.00 mm and thickness of 3.30 ± 0.30 mm. Because of the higher availability of E-PR compared to B-PR, it was possible to prepare much larger gels of E-PR for more accurate measurements, particularly in the low-frequency region. In each series of gels, five samples with different cross-linker concentrations were prepared. The obtained B-SR and E-SR gels were designated B-1 to B-5 and E-1 to E-5, respectively.

Mechanical Measurements. The dynamic viscoelastic 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 (RSAIII, TA Instruments) using a parallel plate geometry. The lower plate was attached to a Petri dish containing water and then placed in an oven at 333 K overnight to quench the reaction. They were then transferred to fresh DMSO and placed 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 significantly during the preceding treatments; swelling and contraction induced changes in thickness of 120% or less. The treated gels of B-SR were square with 9.4 ± 0.30 mm thickness, and the gels of E-SR were cylindrical with a diameter of 20.0 ± 1.00 mm and thickness of 3.30 ± 0.30 mm. Because of the higher availability of E-PR compared to B-PR, it was possible to prepare much larger gels of E-PR for more accurate measurements, particularly in the low-frequency region. In each series of gels, five samples with different cross-linker concentrations were prepared. The obtained B-SR and E-SR gels were designated B-1 to B-5 and E-1 to E-5, respectively.

RESULTS AND DISCUSSION

Characterizations of Polyrotaxanes. Both precursor polyrotaxanes, B-PR and E-PR, were refined and characterized by SEC and 'H NMR. Chromatographs from SEC in Figure 3a showed that each polyrotaxane afforded a single peak with negligible contaminants. The estimations of molecular weights from a calibration curve of PEG standards indicated that B-PR and E-PR had respectively $M_n = 18,900$ and $M_n = 18,200$ and $M_w = 37,200$ and $M_w = 124,000$. These molecular weights were significantly larger than the component axis polymers or rings. The fact that small molecules were not detected under the dilute conditions of SEC identifies the products as polyrotaxanes, rather than pseudopolyrotaxanes that are merely non-end-capped inclusion complexes. The $^1$H NMR spectra of the polyrotaxanes are shown in Figure 3b; all signals were assigned as indicated, with good agreement among the values of the integrals within each component. The ratios of integral values between each of the two components clarify the molar ratio between the rings and the repeating units of the axis polymers.

In E-PR, the molar ratio between α-CD and the PEG monomer unit was 11:89. This corresponded to a weight ratio of 74:26, so the mass content of CD, $w_{CD}$, was 0.74. In B-SR, we employed a six-carbon unit of the main chain of PBD rather than the monomer unit (see Supporting Information for details) because of the complication related to the distribution of unsaturation in PBD. The molar ratio between γ-CD and the six-carbon unit was 23:77, corresponding to a weight ratio of 81:19. Thus, $w_{CD}$ was 0.81.

The obtained mass contents $w_{CD}$ are important characteristic values of polyrotaxanes for obtaining molecular pictures of the networks in slide-ring gels, as will be described later. In addition, the surface coverage (SC), which is a measure of the CD packing density along the axis polymer, is derived from this characteristic value. The SC of a polyrotaxane that has an axis fully covered with CDs is defined to be 100%, and the definitions are based on systematic studies of complexation and molecular modeling. Thus, the SC is also a measure of the slidability: a higher SC indicates lower slidability, and the rings cannot slide at all with 100% SC. Based on a definition in the case of PBD and γ-CD, the SC of the refined B-PR was calculated to be ca. 30%. In a similar way, with a definition established for PEG and α-CD, the SC of the refined E-PR was calculated to be ca. 25% (see Supporting Information for details). These SC values suggest that the CDs of both polyrotaxanes are slidable. B-PR and E-PR were cross-linked in DMSO to yield slide-ring gels, B-SR and E-SR, respectively. The obtained gels were washed to remove unreacted starting materials and immersed in DMSO to achieve equilibrium swelling. All the following results pertain to these refined slide-ring gels in the equilibrium state.

Viscoelastic Behaviors and Curve-Fitting Analyses. Viscoelastic measurements of the series of B-SRs exhibited significant relaxation with a finite equilibrium elastic modulus. Figure 4 shows the frequency dependence of the dynamic
storage Young’s modulus $E'$ and the loss modulus $E''$ of B-SRs with different cross-linker concentrations. Two different plateaus were observed on different time scales. The plateau modulus at the higher frequency increased with the concentration of the cross-linker, whereas the dependence was not very clear at the lower plateau. In addition, the cross-linker concentrations also affected the relaxation dynamics, as can be seen from the shift of peaks for $E''$, indicating a correlation between the relaxation dynamics and the mesh size of the network. For quantitative discussion, we fitted the data using the following equation for the complex modulus $E*$. This is essentially identical to the Havriliak–Negami equation, which has been proven semiempirically and which is usually applied to dielectric relaxations:

$$E*(\omega) = E_\infty - \frac{\Delta E}{(1 + (\omega \tau_{HN})^\alpha)^\beta}$$

(1)

where $\omega$ is the angular frequency, $\Delta E$ is the relaxation strength, $E_\infty$ is the storage modulus $E'$ at the high frequency limit, and $\tau_{HN}$ is the nominal relaxation time. The exponential parameters $\alpha$ and $\beta$ respectively describe the broadness and asymmetry of the spectra. The fitting curves, indicated as the solid lines in the figure, represent the series of data accurately with the parameters shown in Table 1. The fact that $\alpha$ values were close to one indicates the relatively small distribution of relaxation modes, in spite of the large distribution of B-PR molecular weights. The small distribution of relaxation modes was also apparent in the clear maximum of $E''$.

The observed viscoelastic relaxation seems to arise from the peculiar cross-linking manner, not the peculiarities of B-SR such as the hydrophobicity of the axis polymer. As shown in Figure 5, five samples of E-SR with different cross-linker

![Figure 4](image-url)  
Figure 4. Storage and loss Young’s moduli $E'$ and $E''$ of B-SR at 30 °C with different cross-linker concentrations. The solid curves were fitted using eq 1.

Table 1. Fit Parameters for Viscoelastic Relaxations of B-SR

<table>
<thead>
<tr>
<th></th>
<th>$E_\infty$ (kPa)</th>
<th>$\Delta E$ (kPa)</th>
<th>$\tau_{HN}$ (ms)</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-1</td>
<td>109</td>
<td>107</td>
<td>1260</td>
<td>0.960</td>
<td>0.643</td>
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<tr>
<td>B-2</td>
<td>217</td>
<td>213</td>
<td>303</td>
<td>0.873</td>
<td>0.532</td>
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<tr>
<td>B-3</td>
<td>253</td>
<td>249</td>
<td>274</td>
<td>0.938</td>
<td>0.468</td>
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<tr>
<td>B-4</td>
<td>338</td>
<td>334</td>
<td>73</td>
<td>0.956</td>
<td>0.623</td>
</tr>
<tr>
<td>B-5</td>
<td>473</td>
<td>469</td>
<td>48</td>
<td>0.954</td>
<td>0.555</td>
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</table>

![Figure 5](image-url)  
Figure 5. Storage and loss Young’s moduli $E'$ and $E''$ of E-SR at 40 °C with different cross-linker concentrations. The solid curves were fitted using eq 1.

Table 2. Fit Parameters for Viscoelastic Relaxations of E-SR

<table>
<thead>
<tr>
<th></th>
<th>$E_\infty$ (kPa)</th>
<th>$\Delta E$ (kPa)</th>
<th>$\tau_{HN}$ (ms)</th>
<th>$\alpha$</th>
<th>$\beta$</th>
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<tr>
<td>E-l</td>
<td>154</td>
<td>137</td>
<td>3355</td>
<td>0.668</td>
<td>0.439</td>
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<tr>
<td>E-2</td>
<td>228</td>
<td>217</td>
<td>921</td>
<td>0.850</td>
<td>0.532</td>
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<tr>
<td>E-3</td>
<td>242</td>
<td>227</td>
<td>884</td>
<td>0.889</td>
<td>0.563</td>
</tr>
<tr>
<td>E-4</td>
<td>315</td>
<td>300</td>
<td>214</td>
<td>0.813</td>
<td>0.732</td>
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<tr>
<td>E-5</td>
<td>373</td>
<td>352</td>
<td>161</td>
<td>0.797</td>
<td>0.646</td>
</tr>
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</table>
Assignment of Each Plateau and Estimation of Molecular Weights between Cross-Links. In the case of B-SR, the equilibrium Young’s modulus $E_{\text{eq}}$, which was obtained as $E_{\text{eq}} = \Delta E$, was below 5 kPa. The equilibrium moduli were almost 100 times smaller than the moduli at the higher plateau. Such a significant relaxation of modulus is not observed generally in chemically cross-linked materials. Relaxations are observed only when un-cross-linked guest polymers are entangled\textsuperscript{27} or pseudo-cross-links that have finite lifetimes coexist\textsuperscript{28} in permanently cross-linked networks, whereas complete relaxations accompanying macroscopic flows occur in entangled polymers.\textsuperscript{29} To assign the plateaus at different time scales, the average molecular weight between cross-links, $M_x$, was estimated by the simplest description of the Young’s modulus of rubber $E_r$ with an assumption of the affine network, as\textsuperscript{30}

$$M_x = \frac{3 \rho RT}{E_r}$$  \hspace{1cm} (2)

where $\rho$ is the density of the elastic body, $R$ is the gas constant, and $T$ is the absolute temperature. The densities $\rho$, which correspond to the concentration of network that contains the backbone polymers and rings, were obtained from the following equation: $\rho = \rho_0(w_{\text{dry}}/w_{\text{gel}})$, where $w_{\text{dry}}$ is the measured weight of the dried gels, $w_{\text{gel}}$ is that of the swollen ones, and $\rho_0$ is the density of the solvent. Note that the calculation is based on an assumption that the densities of gels are equal to the density of the solvent. Substitution of the values of $E_{\text{eq}}$ into $E_r$ in eq 2 yielded $M_x > 3 \times 10^3$ g/mol; this was much higher than that of the precursor molecule B-PR ($<3 \times 10^4$ g/mol). This means that several tens of B-PRs would form a single partial chain, which is an elastically effective strand in the network. On the other hand, values of $M_x$ that are more probable were obtained by substitution with $E_{\text{cr}}$, as shown in Table 3. To obtain molecular pictures of the network, the average numbers of cyclodextrins between cross-links $n_{\text{CD}}$ can be estimated as

$$n_{\text{CD}} = \frac{M_{\text{CD}}}{M_x}$$  \hspace{1cm} (3)

where $M_{\text{CD}}$ is the molecular weight of the cyclodextrins, ignoring the weight increase due to the cross-linker. The obtained $n_{\text{CD}}$ yields a plausible picture in which one-fifth to one-half of the $\gamma$-CDs function as cross-links, as in the network illustrated in Figure 1. Note that a single E-PR comprises about 10 CDs on average. Thus, it was reasonable to assign the higher plateau as the rubbery one and, therefore, this viscoelastic behavior exhibited a relaxation from the rubbery state to another state in which the modulus was significantly small.

In a similar manner, each plateau of E-SR could be assigned. Based on the assumption that the plateau at the higher frequency was the rubbery one and on the experimental values of $w_{\text{dry}}/w_{\text{gel}}$, eqs 2 and 3 afforded the values of $M_x$ and $n_{\text{CD}}$ shown in Table 4, respectively. These values indicated a plausible picture of the network, similar to that obtained in the case of B-SR. On the other hand, if we assume instead that the lower plateau is the rubbery one, a totally different picture of the network is obtained. The values of $n_{\text{CD}}$ are estimated to be 40–50, meaning that only two cross-linking points exist on average in a single polyrotaxane, because a single E-PR comprises about 90 CDs on average. The estimated cross-linking density would be too low to form an infinite network. In addition, the assumption follows that the elasticity at the higher plateau would arise mainly from pseudo-cross-links and that the relaxation time would be affected by the lifetime of the cross-links. Actually, however, the relaxation times of supramolecular networks are generally almost independent of cross-linking densities.\textsuperscript{31} Thus, it is unlikely that the observed relaxation arises from dissociations of pseudo-cross-links. Therefore, considering all the results together, it is more reasonable to assign the higher plateau as the rubbery one. That is, the viscoelastic behaviors of the series of B-SR and E-SR represent the relaxation of the rubber elasticity and peculiar equilibrium moduli in common.

Relaxation Dynamics Correlated with the Molecular Weight between Cross-Links. The key to elucidating molecular pictures of the relaxation lies in the dynamics that strongly depend on $M_x$. By the assignment of the rubbery plateau and the assumption of the affine network described in eq 2, a single viscoelastic data simultaneously provides both the $M_x$ as molecular-level information and the macroscopic relaxation time. The nominal relaxation time $\tau_{\text{ff}}$ bears the following relationship to the relaxation time $\tau_s$ associated with the maximum of $E''\textsuperscript{32}$

$$\tau_s = \frac{\tau_{\text{ff}}}{\rho_{\text{gel}}} \left[ \frac{\sin \left( \frac{\alpha \pi \tau_s}{2(\beta + 1)} \right)}{\sin \left( \frac{\alpha \pi}{2(\beta + 1)} \right)} \right]^{1/\alpha}$$ \hspace{1cm} (4)

The dependence of the relaxation time $\tau_s$ on $M_x$ is plotted in Figure 6. The relaxation time in each gel series approximately depended on the cube of $M_x$, though the dependence in E-SR was slightly stronger. The cubic power dependence was similar to that predicted by the reptation model of entangled polymers\textsuperscript{28}, except that the reptation time $\tau_d$ depends on the cube of the molecular weight of the polymer chain $M$, not $M_x$. The $\tau_d$ describes the time required for the diffusion of a chain (the probe) along the theoretical confining tube that is formed by surrounding chains (the matrix) with the entire chain length of polymer $L_s$ as shown in Figure 7a. Parts of the probe chain that once diffuse out of the initial tube are considered to lose the orientation anisotropy, which is the origin of stress in the rubbery state, and have no contribution to the macroscopic stress. The theoretical $\tau_d$ describes qualitatively the longest relaxation times in entangled polymers that accompany the macroscopic flow of materials.

### Table 3. Characteristics of the B-SR Series

<table>
<thead>
<tr>
<th>$w_{\text{dry}}/w_{\text{gel}}$</th>
<th>$M_x$</th>
<th>$n_{\text{CD}}$</th>
<th>$\tau_{\text{ff}}$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-1</td>
<td>0.115</td>
<td>8770</td>
<td>5.4</td>
</tr>
<tr>
<td>B-2</td>
<td>0.129</td>
<td>4940</td>
<td>3.1</td>
</tr>
<tr>
<td>B-3</td>
<td>0.143</td>
<td>4690</td>
<td>2.9</td>
</tr>
<tr>
<td>B-4</td>
<td>0.148</td>
<td>3640</td>
<td>2.3</td>
</tr>
<tr>
<td>B-5</td>
<td>0.182</td>
<td>3190</td>
<td>2.0</td>
</tr>
</tbody>
</table>

### Table 4. Characteristics of the E-SR Series

<table>
<thead>
<tr>
<th>$w_{\text{dry}}/w_{\text{gel}}$</th>
<th>$M_x$</th>
<th>$n_{\text{CD}}$</th>
<th>$\tau_{\text{ff}}$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-1</td>
<td>0.097</td>
<td>5440</td>
<td>4.1</td>
</tr>
<tr>
<td>E-2</td>
<td>0.123</td>
<td>4660</td>
<td>3.5</td>
</tr>
<tr>
<td>E-3</td>
<td>0.125</td>
<td>4430</td>
<td>3.4</td>
</tr>
<tr>
<td>E-4</td>
<td>0.139</td>
<td>3780</td>
<td>2.9</td>
</tr>
<tr>
<td>E-5</td>
<td>0.143</td>
<td>3290</td>
<td>2.5</td>
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However, the polymer chains of slide-ring gels cannot flow macroscopically because both ends of the axis polymers are capped with bulky groups. The fact that the relaxation time \( \tau_s \) depends on \( M_c \) indicates that the orientation anisotropy of the chain segments relaxes by a certain local diffusion corresponding to the length of the partial chain \( L_x \). Because of the analogy of dynamics with the entangled polymers, we assumed a theoretical tube on a partial chain as shown in Figure 7c. Similar to the reptation model, only the parts in the tube were considered to contribute to the macroscopic stress.

Consequently, the relaxation times of slide-ring gels reflect the dynamics of the sliding of partial chains, accompanying the relaxation of the orientation anisotropy of the chain segments. Incidentally, the relaxation dynamics of E-SR was slower than B-SR. It would be premature to discuss changes in the dynamics due to the difference of chemical species at this stage, based on the data of only two series of slide-ring gels. Another approach with molecular designs on the slide-ring gels is now in progress, to elucidate and control the relaxation dynamics.

**Contribution of Ring Components to the Equilibrium Modulus.** Although the sliding of partial chains causes the relaxation of stress, these slide-ring gels exhibit finite values of the equilibrium Young’s modulus. The elasticity can be interpreted at the molecular level by the entropy of un-cross-linked CDs. Since CDs slide on the polymer chains on a time scale longer than \( \tau_s \), the CDs exhibit alignment entropy. Although the length of the partial chains varies with the degree of sliding, the number of un-cross-linked CDs between the cross-links remains constant. The densities of CDs that are threaded through shortened partial chains increase with the decrease of entropy, whereas the densities in lengthened chains decrease with the increase of entropy (Figure 8). Thus, the heterogeneous distribution of CDs results in an entropy loss as a whole. If the degree of sliding increases, the entropy of the chains increases and that of the CDs decreases; sliding is unfavorable for CDs, whereas it is favorable for partial chains. Because of the two opposing entropies, the sliding is limited. Therefore, the equilibrium elasticity is attributable to the entropy of both the polymer chains and the CDs. Incidentally, the entropy was recently calculated theoretically.

This interpretation of the equilibrium elasticity should be experimentally evaluated. It is possible to estimate the modulus \( E_{eq} \) by the above-mentioned curve fitting. The estimation, however, will have an uncertainty in its accuracy. Particularly at the lower cross-linking densities, the lower plateaus are not observed, even partially, over the frequency range. In that case, the estimation can hardly avoid excessive extrapolation of the
fitting curves. The equivalent relaxations were confirmed by the linear stress relaxation measurements (see Supporting Information for details). The stress plateaus were observed clearly, indicating the existence of finite equilibrium moduli. It seems that the equilibrium moduli vary slightly compared to the moduli at the rubbery plateaux, though the accuracy of data in the case of B-SR is unsatisfactory. Although the quantitative characterization of the equilibrium modulus will elucidate the full mechanism of these peculiar relaxations, we think that it is premature to discuss it quantitatively relying on these limited numbers of data and samples. Systematic studies on the dependence of the modulus on the cross-linking density are now in progress to elucidate the full mechanism, with consideration of the relaxation dynamics and the nonlinear viscoelasticity.

■ CONCLUSION

We demonstrated herein that two series of slide-ring gels with different axis polymers exhibited peculiar viscoelastic relaxations and equilibrium elasticities. Regardless of the axis polymers, the relaxation times exhibited a cubic power dependence on the molecular weights of the partial chains. By analogy to the dynamics of entangled polymers, the relaxation reflected the sliding dynamics of partial chains through the figure-eight cross-links. At the same time, the insight into the sliding dynamics enabled us to discern a possible contribution by the entropy of the ring components to the equilibrium elasticity. The hypothesis that the elasticity originates from two opposing entropies, which arise from chains and rings respectively, can explain the contradiction that the slide-ring gel remains an elastic body despite the relaxation of the orientation anisotropy of the chain segments. The hypothesis requires additional experimental verification, but we think that it may quickly lead to the possible design of new functional materials.

■ ASSOCIATED CONTENT

* Supporting Information Calculations of $w_{ex}$ and SC of polyrotaxanes and linear stress relaxation data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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