SANS Studies on Deformation Mechanism of Slide-Ring Gel

Takeshi Karino,[†,§] Yasushi Okumura,[‡,§] Changming Zhao,[‡,§] Toshiyuki Kataoka,[‡] Kohzo Ito,[‡,§] and Mitsuhiro Shibayama*[,†,§]

Neutron Science Laboratory, Institute for Solid State Physics, University of Tokyo, Tokai, Ibaraki, 319-1106, Japan; Graduate School of Frontier Sciences, University of Tokyo, Kashiwa, Chiba 277-8561, Japan; and CREST, Japan Science and Technology Agency, 4-1-8 Honcho Kawaguchi Saitama, 332-0012 Japan

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ABSTRACT: The deformation mechanism of "slide-ring" (SR) gels was investigated with small-angle neutron scattering (SANS). The SR gels were prepared by coupling α-cyclodextrin (CD) molecules on polyrotaxane chains consisting of poly(ethylene glycol) and CD. Because of a hollow structure of CD molecules, the cross-links made of CD molecules in a figure-of-eight shape can slide along the polymer chain. A normal butterfly pattern was observed for the first time in two-dimensional SANS isointensity profiles for the SR gels under uniaxial deformation, where the normal butterfly pattern means a prolate isointensity pattern in the direction perpendicular to the stretching direction. However, by either increasing the cross-link density or increasing the stretching ratio, the normal butterfly patterns changed to abnormal butterfly patterns as are commonly observed in conventional covalent-bonded chemical gels. The difference in the deformation mechanism as well as the cross-linking inhomogeneities between the SR gels and the covalent-bonded chemical gels is discussed by focusing on the unique architecture of the SR gels.

Introduction

Polymer gels are three-dimensional polymer networks consisting of polymer chains, cross-links, and a large amount of solvent. Although cross-links are introduced by covalent or physical bonding, the cross-links are inhomogeneously distributed in the space. As a matter of fact, various types of inhomogeneities of cross-links have been observed by scattering methods, such as small-angle X-ray, neutron, and light scattering.[1−6] In general, the scattering intensity of polymer gels increases with increasing cross-link density in small-angle region.[1] This means that spatial inhomogeneities increase by introducing cross-links in polymer gels. Inhomogeneities are also observed by dynamic light scattering (DLS) measurements as nondecaying component in the time−intensity correlation function as well as speckle patterns.[5,6]

The gel inhomogeneities are amplified by stretching and the so-called butterfly pattern appears.[7−12] Butterfly patterns are two-lobe isointensity scattering patterns. Butterfly patterns are also observed in polymer solutions in a flow field.[13,14] The scattering theory predicts a prolate pattern elongated in the perpendicular direction to the stretching direction of polymer chains. The appearance of a butterfly pattern in stretched polymer films indicates a deformation of labeled polymer chains along the stretching direction.[15,16] However, unlike the case of a deformation of labeled polymer chains, the scattering patterns for stretched gels are prolate in the direction to the stretching direction. This is why such a pattern is called an "abnormal butterfly pattern".[9,11,17] Abnormal butterfly patterns in polymer gels were reported by Mendes for polystyrene[8] and polyelectrolyte gels,[10] by Ramzi for polystyrene,[18] and by Shibayama et al. for thermosensitive weakly charged gels.[12] The butterfly patterns are theoretically explained by Onuki,[19,20] Rabin et al.,[21] and Panyukov and Rabin.[22] According to these theories, the scattering function of polymer gels is divided into two terms. One is a Lorentz-type scattering function (equivalent to an Ornstein−Zernike function) representing thermal fluctuations. The other is a squared-Lorentz-type function corresponding to the static frozen inhomogeneities. If the spatial inhomogeneities do not exist, the butterfly pattern is reduced to a normal butterfly pattern, similar to the case of a stretching of labeled chains. The theories concluded that abnormal butterfly pattern is ascribed to an increase of the spatial inhomogeneities in the stretching direction. However, as will be discussed in this paper, an opposite type of butterfly pattern, i.e., a normal butterfly pattern having two lobes in the direction perpendicular to the stretching direction, was observed for the first time in a slide-ring gel.

Okumura and Ito developed a new type of gel called a topological gel or a slide-ring gel having mobile cross-links.[23] Hereafter, we call this type of gel slide-ring gel (SR gel). The novelty of the SR gel is addressed by Granick and Rubinstein.[24] The SR gels consist of polyrotaxane made of α-cyclodextrin (CD) and poly(ethylene glycol) (PEG). Polyrotaxane is one of a supramolecule composed of PEG chains threading into CD molecules. Thus, CD molecules can move freely along the PEG chains. These SR gels were synthesized by cross-linking between CDs. The static structure factors of the SR gels as well as their dynamics in solutions were investigated by small-angle neutron scattering (SANS), and the following important findings were disclosed.[25] (1) The polyrotaxane chains in deuterated dimethyl sulfoxide (d-DMSO) take a rodlike conformation, whereas a Gaussian chain in NaOD aqueous solution ($NaOD_{aq}$). (2) The degree of inhomogeneities of a SR gel in $NaOD_{aq}$ has a minimum around the sol−gel transition, whereas that in d-DMSO increases monotonically with increasing cross-linker concentration. (3) the scattering func-

† Institute for Solid State Physics, University of Tokyo.
‡ Graduate School of Frontier Sciences, University of Tokyo.
§ CREST, Japan Science and Technology Agency.
* To whom correspondence should be addressed. E-mail: sibayama@issp.u-tokyo.ac.jp.

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tion, $I(q)$, of the SR gel in $NaOD_{aq}$ can be described by a Lorentz function, while that in d-DMSO is given by the sum of a squared-Lorentz function and a scattering function for a rod. Here, the "degree of inhomogeneities" is defined as the ratio of the zero-scattering intensity, $I(q=0)$, of the gel to that of the corresponding polymer solution. These differences in $I(q)$ are ascribed to the difference in the stacking behavior of CD molecules on PEG chains in the SR gels.

The mobile cross-links in the SR gels may reduce spatial inhomogeneities of the gels due to rearrangement of the distribution of cross-links. In the previous paper,[25] we discussed the static structure factor of SR gels in both $NaOD_{aq}$ and d-DMSO solutions, and we did not investigate the mobility of cross-links in the SR gels. It is expected that the spatial inhomogeneities of SR gels could be suppressed by sliding the cross-links. In this study, SANS measurements were carried out to demonstrate pieces of evidence of the sliding motion and to elucidate the deformation mechanism of SR gels under uniaxial deformation. As will be shown in this paper, the observation of (1) a normal butterfly pattern and (2) a transition from normal to abnormal butterfly patterns is strong evidence of the unique feature of the SR gels and high potential of material applications, such as biomaterials (soft contact lens, artificial crystalline), cosmetic, polymer battery, fuel cell, and soft actuator.

Theoretical Background

Among various models and/or theories to describe the scattering functions for deformed gels, the following three models seem to be appropriate for the discussion of the physical implication of the deformation mechanism of gels: (a) frozen-blob cluster model,[7] (b) Onuki model,[19] and (c) Panyukov−Rabin model.[22,26] All of these theories assume the presence of frozen inhomogeneities introduced by random cross-linking. Since frozen inhomogeneities arise from permanent cross-links, these theories are not applicable to the deformation of SR gels. Here, we briefly address the Onuki theory for the discussion of the cross-linking effects on the scattering intensity as well as the anisotropy.

The structure factor for deformed gels is given by[19,27]

$$I(q) \sim \frac{\phi^2 kT}{M_{os}(\lambda,\beta)} \frac{1}{1+\dfrac{C\phi^2 q^2}{M_{os}(\lambda,\beta)}}\left[1 + p(q)\left(\frac{\mu}{M_{os}(\lambda,\beta)}\right)\frac{[J(\beta)-(\phi_0/\phi)^{-2/3}]^2(\phi_0/\phi)^{2/3}}{1+\dfrac{C\phi^2 q^2}{M_{os}(\lambda,\beta)}}\right] \quad (1)$$

where $M_{os}(\lambda,\beta)$ is the direction-dependent osmotic modulus, p is the degree of irregularity, C is a constant related to the concentration gradient, and ϕ_0 and ϕ are the volume fraction at the preparation and at the observation conditions. $M_{os}(\lambda,\beta)$ and $J(\beta)$ are given by

$$M_{os}(\beta) \equiv K + \frac{1}{3}\mu + \mu J(\beta), \quad J(\beta) = \left(\lambda^2 - \frac{1}{\lambda}\right)\cos^2\beta + \frac{1}{\lambda} \quad (2)$$

where K and μ are the bulk modulus and shear modulus of the gel, respectively.[27] In the case that the cross-links are randomly distributed in the space obeying a Poisson distribution, $p(q)$ can be set as a constant, i.e., $p(q) = p_{int}$.

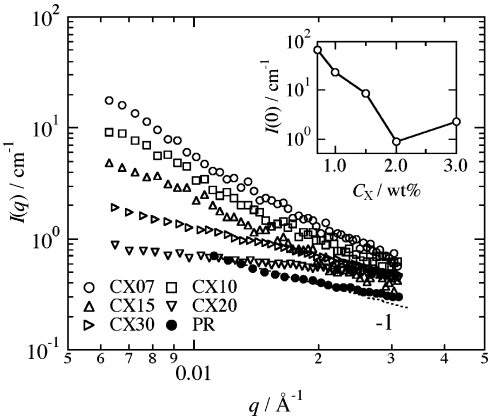

Figure 1. Scattering intensity, $I(q)$, of the SR gels in d-DMSO with various cross-link concentrations, C_xs. $I(q)$ decreases with increasing C_x, which is opposite to the case of conventional covalent-bonded chemical gels. The filled circles with the line denote $I(q)$ for the precursor of the SR gel, i.e., polyrotaxane solution in d-DMSO. The inset shows the C_x dependence of $I(0)$.

Not only the Onuki theory but also all of other theories discussed above take into account the frozen inhomogeneities inherent of polymer gels. However, the q dependence is different from each other. In the case of the frozen-blob cluster model,[7] the asymptotic behavior of $I(q)$ at a low q-region is essentially a Lorentz function with a correlation length of ξ, i.e., $I(q) \sim (1 + \xi^2 q^2)^{-1}$. Hence, the expected asymptotic behavior is $I(q) \sim q^{-2}$. On the other hand, both the Onuki model and the Panyukov−Rabin model have a squared-Lorentzian term in addition to a Lorentz function. This squared-Lorentzian term accounts for both inhomogeneities and anisotropy by stretching. According to Mendes et al.,[11] however, none of these theories are able to describe quantitatively the large range of deformations. Ramzi and co-workers studied the butterfly patterns of randomly cross-linked[28] and end-linked polystyrene networks.[18] Here, the behaviors of free chains embedded in the network were also considered. The agreement between the experiments and the theories, however, was again poor. It is rather surprising to learn that strong inhomogeneities are also present even in an end-linked polymer network. They attributed this to imperfect chemistry or to physical origins, such as entanglement or large loops. In any case, these theories are not applicable to the deformation of SR gels since frozen inhomogeneities arise from permanent cross-links. Hence, we employ a more phenomenological model to describe the deformation of the SR gels.

In the previous study on SR gels in d-DMSO, another kind of scattering function was introduced in order to reproduce the observed scattering functions, which are a combination of a squared-Lorentz function and a scattering function for randomly oriented thin rod, i.e.

$$I(q) = \frac{I_{SL}(0)}{(1+q^2\Xi^2)^2} + I_R(0)q^{-1} \quad (3)$$

where $I_{SL}(0)$ and $I_R(0)$ are the forward scattering intensities of the squared-Lorentz and the rod, respectively. Ξ is the characteristic length of gel inhomogeneities. The physical meaning of eq 3 is as follows. The first term of the right-hand side shows the spatial inhomogeneities of the gels or two-phase separated structure.[19] This term is identical to the Debye−Bueche

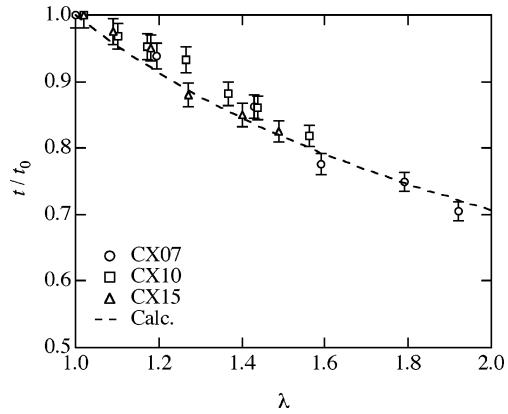

Figure 2. Elongation ratio, λ, dependence of the normalized sample thickness, t/t_0, of the SR gel films. The dashed line indicates the calculated line with the assumption of a constant-volume deformation.

function.[29] The second term describes rodlike chains as a local structure of gels. Note that CD molecules on PEG are stacked together in DMSO because of strong hydrogen-bonding capability as was revealed in the previous paper.[25] Note that the Lorentzian term is missing in eq 3. This is due to the fact that the polyrotaxane chains in d-DMSO are rodlike as a result of stacking of CD molecules.[25]

Experimental Section

Preparation of Slide-Ring Gels. The preparation of polyrotaxane and the slide-ring gel is described in more detail elsewhere.[30] 0.9 g of poly(ethylene glycol) (PEG) and 3.6 g of α-cyclodextrin (α-CD) were dissolved in 15 g of water at 80 °C and kept at 5 °C overnight to yield white paste. The molecular weight of PEG was 1.0×10^5. The paste was dried, followed by addition of an excess of 2,4-dinitrofluorobenzene together with dimethylformamide (DMF). The mixture was stirred in a nitrogen atmosphere at room temperature overnight and then was dissolved in DMSO and precipitated twice from a 0.1% sodium chloride aqueous solution to give a yellow product. The product was collected, washed with water and methanol, and dried to produce the polyrotaxane. The filling ratio (*FR*), i.e., the weight percentage of CDs included on a PEG chain, was determined by ^{1}H NMR. The number of CD calculated form the peak height of CD and PEG. It is noteworthy that a CD molecule can be stoichiometrically included per 2 PEG monomer units (i.e., $FR = 100\%$). The filling ratio of CD was 17%.

Slide-ring gels were prepared in deuterated dimethyl sulfoxide (99.9% deuteration) (d-DMSO), where *N,N′*-carbonyldiimidazole was used as cross-linker. Five cross-linker concentrations, C_X, were chosen to be 0.7, 1.0, 1.5, 2.0, and 3.0 wt % with respect to the polyrotaxane solution. The concentration of the polyrotaxane was 10 wt %. Accordingly, the sample codes were defined as CX07, CX10, CX15, CX20, and CX30.

Small-Angle Neutron Scattering. Small-angle neutron scattering (SANS) experiments were carried out at the SANS-U spectrometer at Institute for Solid State Physics, University of Tokyo, Tokai, Japan. Two-dimensional scattering intensity patterns were collected with a two-dimensional detector (64 × 64 cm^2) placed at 8 m position from the samples. The incident neutron wavelength was 7.0 Å. The observed scattered intensity functions were corrected for air scattering, incoherent scattering, and transmission and then were rescaled to the absolute intensity, $I(q)$, with a polyethylene (Lupolen) secondary standard.

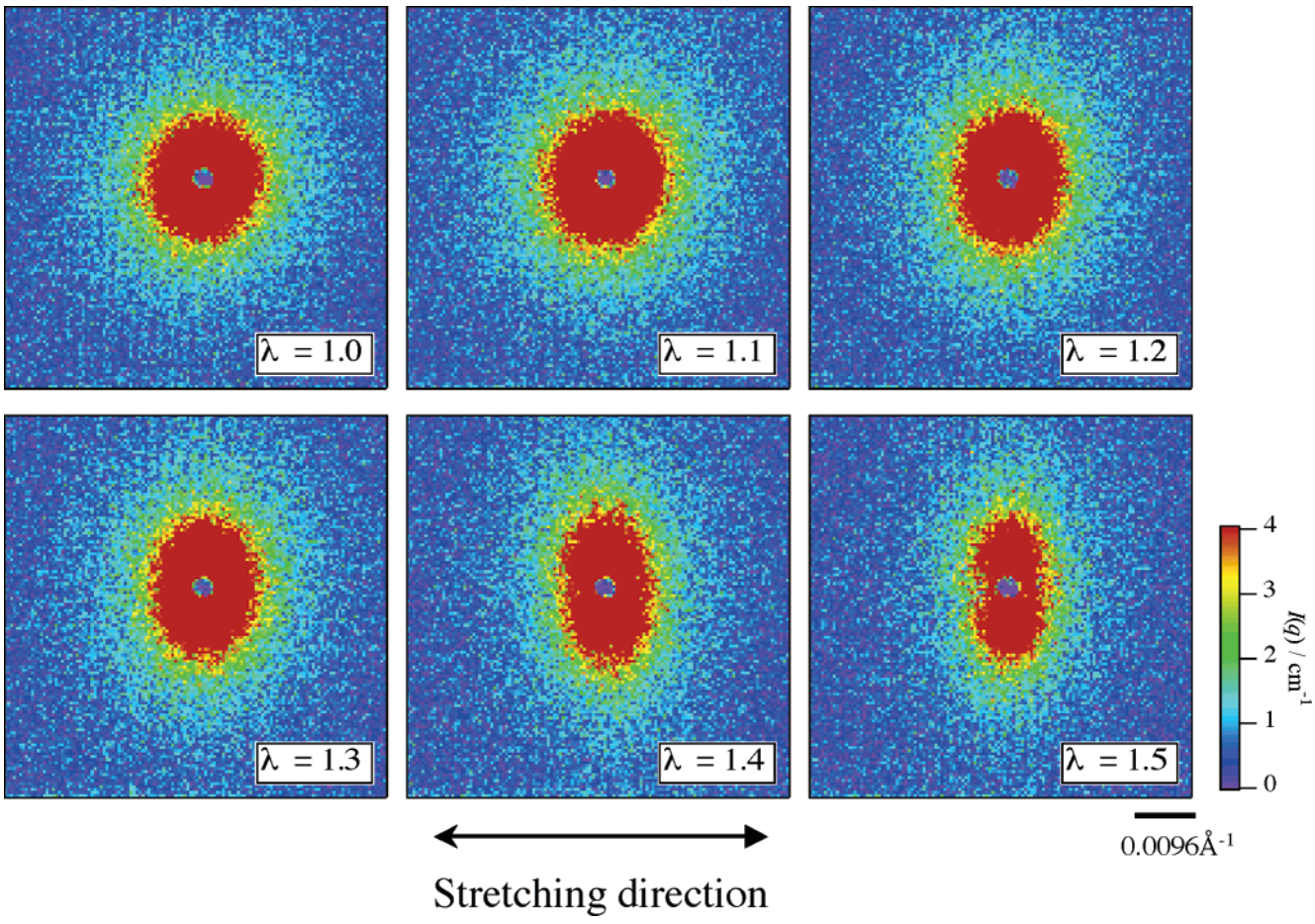

Figure 3. SANS isointensity patterns of the SR gel (CX10) with various stretching ratios, λ's. The stretching direction is horizontal.

Results and Discussion

Scattering Intensity of Undeformed SR Gels. Figure 1 shows the cross-link concentration dependence of scattering intensity, $I(q)$, for undeformed SR gels (open symbols) and for polyrotaxane solution (filled circles). $I(q)$ for the polyrotaxane can be scaled as $I(q) \sim q^{-1}$ (dashed line). This indicates that polyrotaxane chains are in a rodlike form in d-DMSO as a result of stacking of CD molecules.[25] Now, let us discuss the C_x dependence of $I(q)$. In general, $I(q)$ for polymer gels increases with increasing the cross-link density.[31] This is due to the fact that cross-linking introduces frozen inhomogeneities, leading to an increase in $I(q)$ with cross-links density. However, interestingly enough, $I(q)$ of the SR gels decreased with increasing C_x up to $C_x =$ 2.0 wt %, as shown in Figure 1. These results suggest that the concentration fluctuations of the SR gel are suppressed by an introduction of cross-links. Here, let us discuss the C_x dependence of $I(q)$ with the Onuki theory. According to eq 1, the zero-q scattering intensity for an undeformed gel ($\lambda = 1$) is given by

$$I(q=0) \approx \frac{\phi^2 kT}{M_{os}(\beta)} = \frac{\phi^2 kT}{M_{os}}\left(1 + p_{int}\frac{\mu}{M_{os}}\right) \qquad (4)$$

With increasing C_x, both M_{os} and p_{int} increase since the bulk modulus, K, and the shear modulus, μ, are increasing function of C_x (see eq 2). In the case of covalently bonded chemical gels, the effect of increasing p_{int} is larger than that of M_{os}. Hence, $I(q)$ is expected to increase with increasing C_x. The Young's modulus of the SR gels also increases with increasing C_x.[30] Accordingly, M_{os} is expected to increase as is the case of covalently bonded chemical gels. Therefore, the decrease in $I(q)$ in the SR gels may be ascribed to an increase in M_{os} without noticeable increase in p_{int}, i.e., inhomogeneities, at low C_x's. As a matter of fact, the SR gels have the lowest degree of inhomogeneities at $C_x \approx 2.0$ wt % (see the inset of Figure 1). Therefore, the SR gels with low C_x's have very low inhomogeneities owing to "slidable" cross-links.

Scattering Intensity of Stretched SR Gels. Figure 2 shows the variation of the normalized sample thickness as a function of the stretching ratio, λ. The deformation was completely reversible in this range of stretching. The details of mechanical properties are discussed elsewhere.[30] The dashed curve indicates the theoretical prediction with the assumption of no-volume change, i.e., the Poisson ratio being 0.5. This is the case of ideal rubber deformation

$$t/t_0 = \lambda^{-1/2} \qquad (5)$$

As shown in the figure, all the data points fall on the calculated curve (the dashed line) irrespective of the cross-link density, indicating that the SR gels obey the rubber deformation.

Figure 3 shows the two-dimensional SANS isointensity patterns of deformed SR gels (CX10). The stretching direction was horizontal. As clearly shown, the scattering patterns at $\lambda = 1.0$ are isotropic but become elliptic by increasing λ with the long axis perpendicular to the stretching direction. This type of scattering pattern is called a normal butterfly pattern, as was introduced in Introduction. This is the first time to our knowledge to observe a normal butterfly pattern in a polymer gel. As is well-known, conventional chemical gels show abnormal butterfly patterns in which the scattering intensity increases in the parallel direction.[7−12] The origin of the appearance of abnormal butterfly patterns is explained by inhomogeneities. Polymer gels inherently possess cross-link inhomogeneities. However, these inhomogeneities are implicit in the state of preparation because topological inhomogeneities introduced by cross-links are buried by concentration fluctuations of the polymer chains. The inhomogeneities, however, become explicit by deformation, such as swelling, stretching, or compression.[7,11,32] The SR gels, on the other hand, were found to exhibit normal butterfly patterns. This is strong evidence of the presence of sliding cross-links that effectively lower the inhomogeneities.

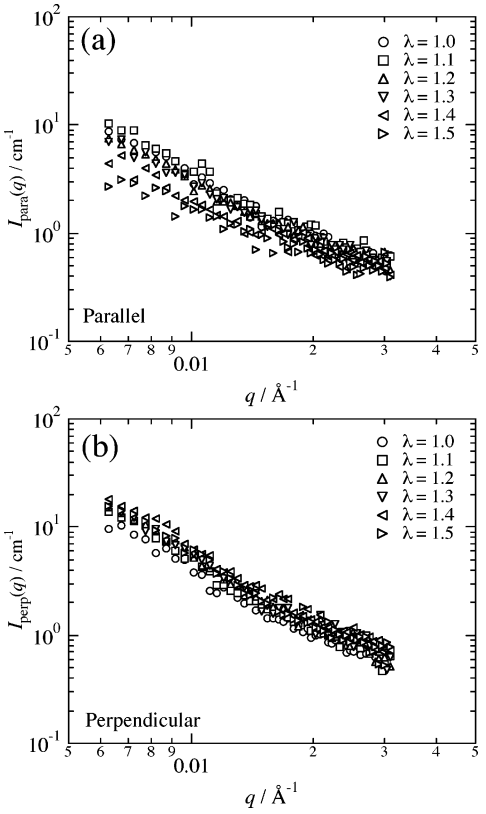

Figure 4. Sector-averaged $I(q)$'s of the SR gel (CX10) stretched in (a) the parallel and (b) perpendicular directions.

Figure 4 shows the sector-averaged scattering intensities of the butterfly patterns shown in Figure 3. The sector angle was 10° in both the parallel (para) and the perpendicular (perp) directions. Note that $I_{para}(q)$ decreases, while $I_{perp}(q)$ remains more or less invariant with increasing λ. In the previous paper, the scattering function of nondeformed SR gels in d-DMSO were well fitted with a sum of a squared-Lorentz and a rod functions given by eq 3.[25] Here, the same equation was employed to reproduce the experimentally obtained scattering functions.

As shown in Figure 5, the fitting results agree well with the observed ones at least for $q \leq 0.015$ Å^{-1}. Note neither undeformed nor deformed gels could not be reproduced by the Onuki scattering function (eq 1) for $q > 0.015$ Å^{-1} as shown with the dashed lines in the figure. The Onuki scattering function tails with a Lorentz function with an asymptote of $I(q) \sim q^{-2}$, while the observed one is given by $I(q) \sim q^{-1}$. The reason for this discrepancy may arise from the specific feature of the SR gels in DMSO, where CD molecules have a

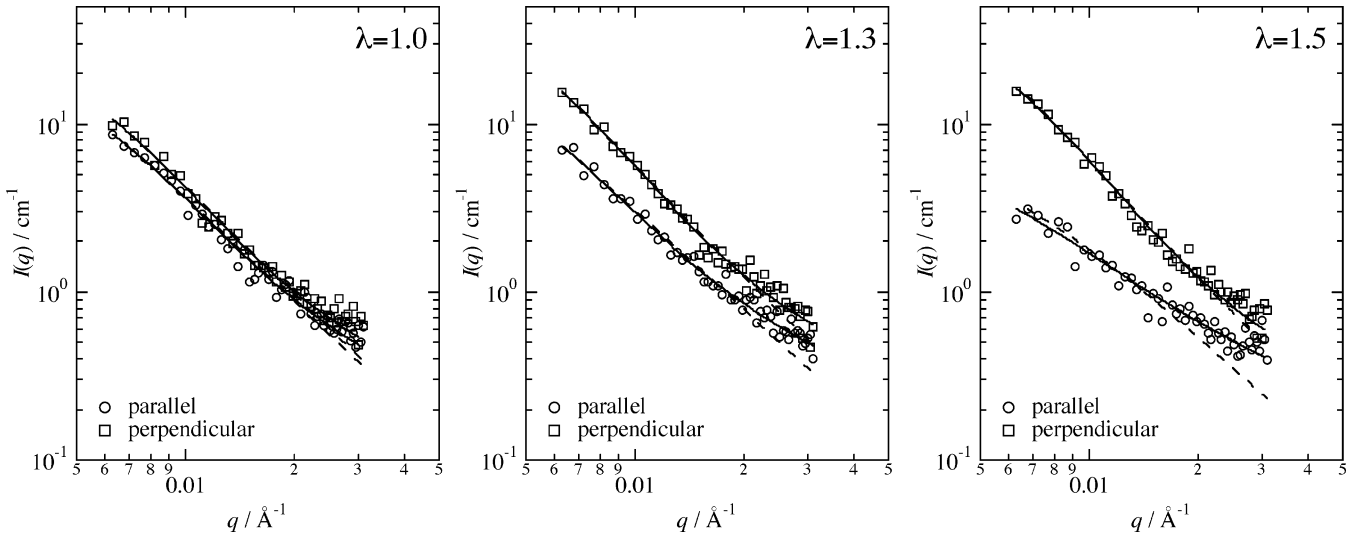

Figure 5. Results of curve fitting with the sector-averaged $I(q)$'s of the SR gel (CX10): (a) $\lambda = 1.0$, (b) $\lambda = 1.3$, and (c) $\lambda = 1.5$.

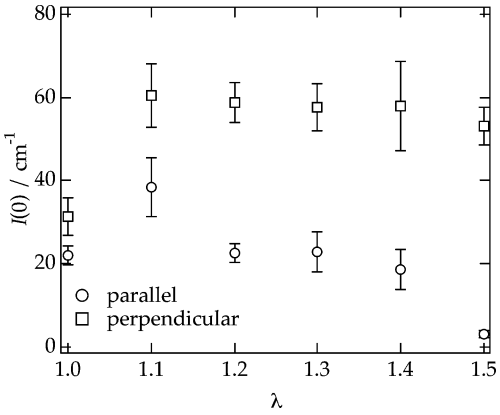

Figure 6. Stretching ratio dependence of $I(0)$ for the SR gel (CX10) in the parallel (circles) and perpendicular directions (squares).

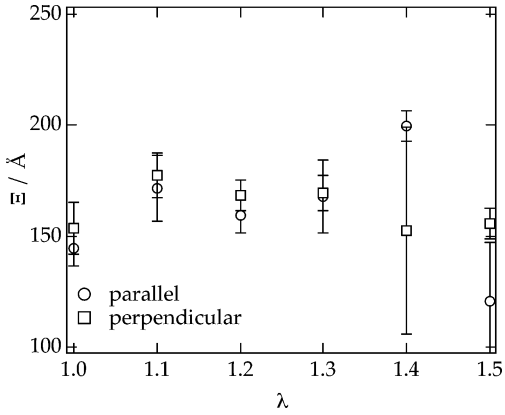

Figure 7. Stretching ratio dependence of Ξ for the SR gel (CX10) in the parallel (circles) and perpendicular directions (squares).

tendency to stack each other and the polyrotaxane chain becomes a stiff rod. We reported that the polyrotaxane chains behave as Gaussian chains in a $NaOD_{aq}$.[25] A crossover from the Debye−Bueche ($\sim q^{-4}$) to q^{-1} behavior appeared at $q \approx 0.015$ Å^{-1}. The difference in $I(q)$s between the perpendicular and parallel directions becomes larger as λ increases, indicating an increase in anisotropy.

Figure 6 shows the variations of the fitted values of $I(0)$ for CX10. The data indicate that $I_{para}(0)$ and $I_{perp}(0)$ show a jumpwise increase at $\lambda = 1.1$. This may due to a structural reorganization of the gel since an as-prepared gel film was stretched. With further increasing λ, $I_{para}(0)$ decreases while $I_{perp}(0)$ remains constant within the experimental accuracy.

Figure 7 shows the variation of Ξ as a function of λ. Interestingly, Ξ_{para} (circles) is decreasing and Ξ_{perp} (squares) remains constant with respect to λ. Here, Ξ is the frozen-blob correlation length ($= \xi_c$) as was introduced by Bastide et al.[7] Note that Mendes et al. employed an Ornstein−Zernike function to describe the scattering function for deformed polymer gels and obtained a decrease of $\xi_{c,perp}$ in the perpendicular direction and an increase of $\xi_{c,para}$ in the parallel direction. However, the fitting itself was not successful. They ascribed this failure to be inadequacy of the theories. We guess, however, that it is due to a mischoice of the scattering function to apply. As mentioned above, we employed a combination of a squared-Lorentz function and a rod function. The reasons of the employment of the squared-Lorentz function lie on the presence of inhomogeneities in the SR gels prepared in d-DMSO as discussed above. Apart from this argument, it is clear that our result on the λ dependence is completely opposite to that obtained by Mendes et al.[11] Since the size of structural inhomogeneities, i.e., Ξ, of conventional gels increases with λ at least in the stretching direction, this experimental evidence again suggests that SR gels are very different from conventional chemical gels.

Normal-to-Abnormal Transition of Butterfly Pattern. Figure 8 shows the isointensity scattering patterns of CX10 ($C_x = 1.0$ wt %) (upper) and CX20 ($C_x = 2.0$ wt %) (lower). As clearly shown in the figure, the scattering intensity for CX20 is much lower than that of CX10. This is in accordance with the statement given in Figure 1. More interestingly, CX20 shows "abnormal" butterfly patterns with increasing λ. This is again the first observation of a normal-to-abnormal butterfly pattern transition.

Deformation Model of SR Gels. On the basis of the experimental findings described above, we propose a deformation mechanism of the SR gels. Figure 9 shows the comparison of the deformation mechanism of polymer gels. In the case of covalently bonded chemical gels, cross-links are nonrandomly distributed in a unde-

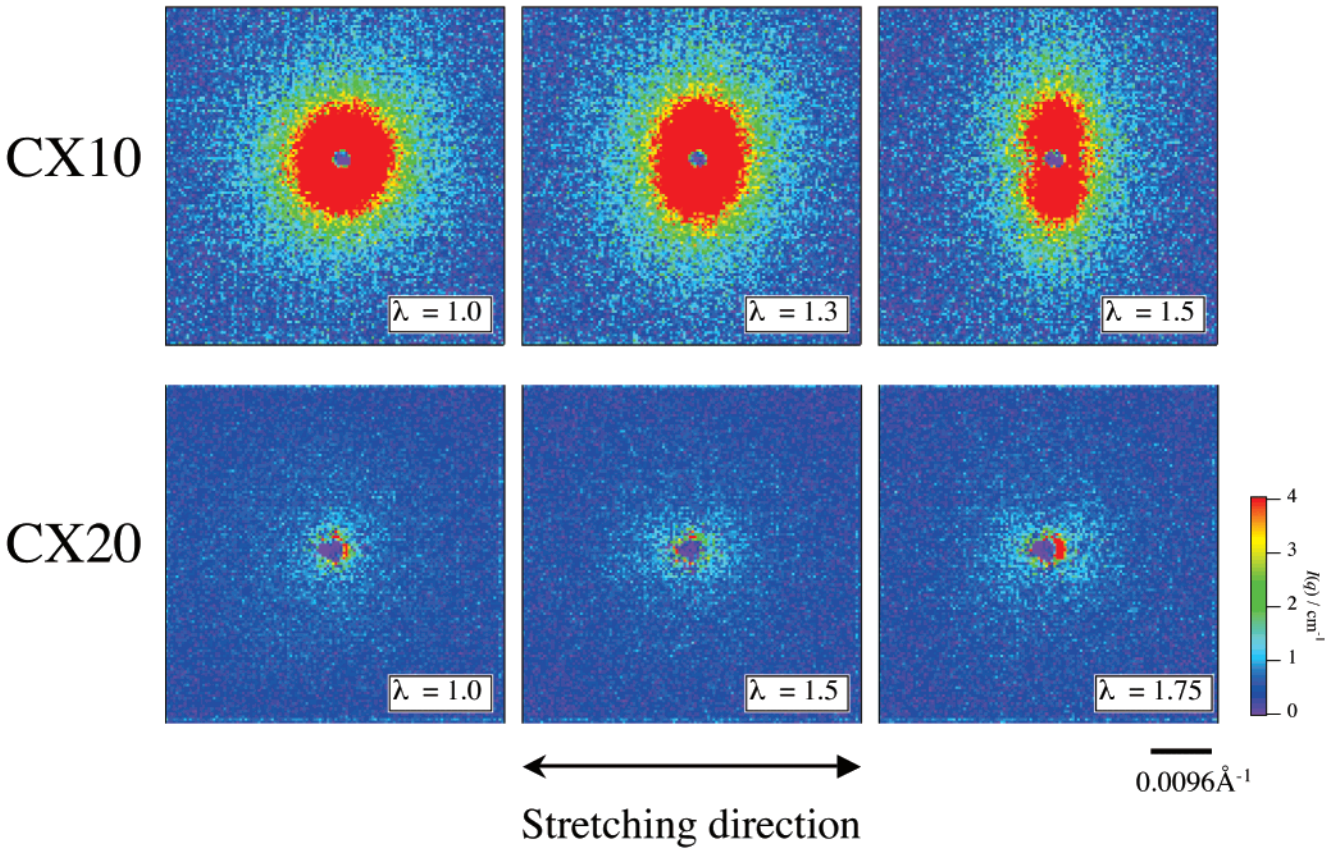

Figure 8. SANS isointensity patterns of the SR gel with CX10 ($C_x = 1.0\%$) and CX20 ($C_x = 2.0\%$). Upon stretching, CX10 exhibits normal butterfly patterns, while CX20 does abnormal butterfly patterns.

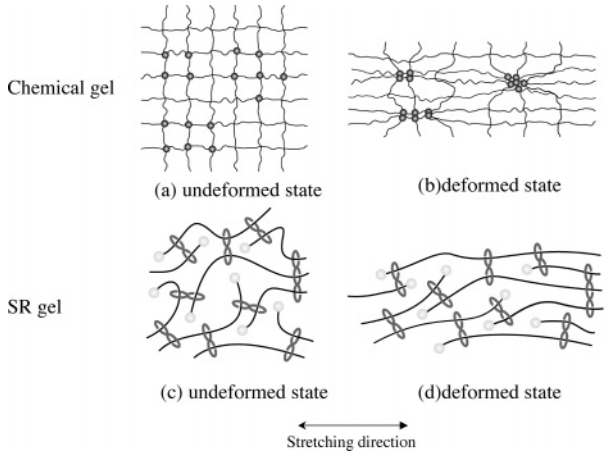

Figure 9. Schematic models showing deformation mechanism for (a, b) covalently bonded chemical gels and (c, d) slide-ring (SR) gels.

formed polymer gel (Figure 9a). The cross-link inhomogeneities preferentially increase in the stretching direction. By stretching, polymer chains are stretched and oriented in the stretching direction. However, frozen blobs are displaced along the stretching direction without changing their shapes significantly (Figure 9b). This means that the spatial inhomogeneities of chemical gels increase in the stretching direction, resulting in an appearance of an abnormal butterfly pattern. On the other hand, the spatial inhomogeneities of SR gel do not increase in the stretching direction since the cross-links can move freely along the polymer chain (Figure 9c,d). This is why a normal butterfly pattern was observed. As shown in Figure 8, a highly cross-linked SR gel, i.e., $C_x = 2.0$ wt %, shows an abnormal butterfly pattern by stretching. This indicates that the sliding cross-links with a high C_x do not move effectively to reduce the spatial inhomogeneities.

Conclusion

Small-angle neutron scattering experiments were carried out in order to elucidate the mobility of cross-links of slide-ring gels (SR gels) under uniaxial deformation. Four interesting findings were disclosed in this study. (1) The SR gels obey rubberlike deformation with zero-volume change by stretching. This means that the SR gels can be regarded as typical rubbers where energy loss by stretching is negligible. (2) Surprisingly, the scattering intensity decreases with increasing C_x. This indicated that the spatial inhomogeneities decreased with increasing C_x. This behavior has not been observed in the conventional chemical gels and is the first observation in gels. (3) A normal butterfly pattern was observed for the first time. Under uniaxial stretching, the isointensity scattering intensity curve shows a normal butterfly pattern. The scattering intensity perpendicular to the stretching direction did not noticeably change by stretching. On the other hand, in the parallel direction, the scattering intensity decreased with increasing λ. This suggested that the spatial inhomogeneities of the SR gel did not increase by stretching. These results imply that the cross-links of the SR gels move along to the polymer chain. (4) By increasing C_x from $C_x = 1.0$ to 2.0 wt %, a normal-to-abnormal butterfly pattern transition took place. This suggests that the characteristic feature of the SR gels, i.e., the presence of slidable cross-links, is deteriorating by increasing the cross-link density. All of the above

findings strongly support the "mobile" cross-links and their unique behavior in uniaxial stretching.

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