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SANS Studies on Spatial Inhomogeneities of Slide-Ring Gels

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ABSTRACT: Slide-ring gels (SR gel) [previously termed as topological or polyrotaxane gels: Okumura, Y.; Ito, K. *Adv. Mater.* **2001**, *13*, 485] have remarkable physical properties, such as large extensibility and mechanical strength. The SR gels are cross-linked polyrotaxane (PR) consisting of poly(ethylene glycol) (PEG) chains and α-cyclodextrin (CD), in which the cross-linkers are made of CD dimers and capable of sliding along the PEG chains. To elucidate the physical picture and properties, the scattering functions, $I(q)$s, of SR gel in NaOD aqueous solutions ($\mathrm{NaOD_{aq}}$) and in deuterated dimethyl sulfoxide (d-DMSO) were investigated by small-angle neutron scattering (SANS) and were compared with those of pregel solutions, where q is the magnitude of the scattering vector. The following facts were disclosed: (1) The polyrotaxane chains take a rodlike conformation in d-DMSO, whereas a Gaussian chain in $\mathrm{NaOD_{aq}}$. (2) The degree of inhomogeneities of SR gel in $\mathrm{NaOD_{aq}}$ has a minimum around the sol−gel transition, whereas that in d-DMSO increases monotonically with increasing cross-linker concentration. (3) $I(q)$ of SR gel in $\mathrm{NaOD_{aq}}$ 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. These differences in $I(q)$ are ascribed to the difference in the stacking behavior of CD molecules on PEG chains in PR.

Introduction

Polymer gels consist of flexible polymer chains slightly cross-linked to each other. Because of the presence of cross-links, the gel does not dissolve in a solvent but swells or collapses depending on the affinity of the network polymer chains to the solvent.[1] Polymer gels are roughly classified to either chemical gels or physical ones. The chemical gels are cross-linked via covalent bonds. Hence, the cross-links of the network are permanent and fixed. On the other hand, the physical gels are cross-linked via noncovalent junctions, such as microdomains, helices, and microcrystallines, etc., and undergo sol−gel transition upon changes of environmental parameters like temperature and pH.[2] One of the characteristic features of gels, which can also be a disadvantage, is the presence of spatial inhomogeneities. The inhomogeneities are inherent in polymer gels and are of particular significance in chemical gels.[3] Since most of chemical gels are made from radical polymerization of monomer and cross-linker, the resultant gel is a kind of assembly of finite microgel clusters tied together.[4] These types of inhomogeneities degrade the physical properties of gels, namely, loss of clarity, low deformability, fragility, low swelling ratio, low mechanical strength, etc.[5] Although radiation cross-linking is one of the methods to circumvent these disadvantages, inhomogeneities are inevitably introduced because the cross-linking itself is a chemical reaction.[6,7]

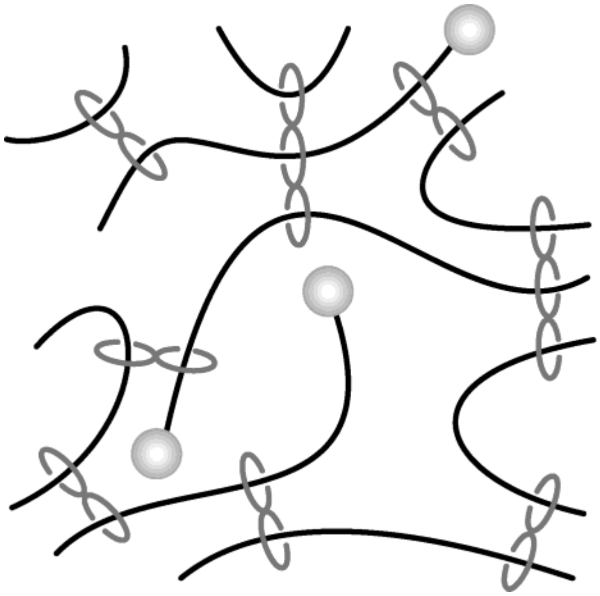

Figure 1. Illustration of slide-ring gel. PEG chains are cross-linked with double- and/or triple-ring cross-linkers made of α-cyclodextrin dimers and/or trimers. The chain ends are blocked with a bulky end groups so as to keep the cross-links on the chains.

Recently, another type of gels has been developed, which is a slide-ring gel.[8] The slide-ring gel has mobile cross-links that can slide along the backbone polymer chains. Figure 1 shows an illustration of slide-ring gel, in which double- and/or triple-ring cross-linkers are able to slide along polymer chains. These mobile cross-links allows (1) high extensibility, (2) large degree of swelling, and (3) large reversible deformability. Realization of slide-ring gels can be achieved by using polyrotaxane. Polyrotaxanes are prepared by threading linear polymer chain onto cyclic molecules. The linear polymer chain goes through the ring molecule like a thread and a bead. One of the most typical polyrotaxanes is made of poly(ethylene glycol) (PEG) and α-cyclodextrin (CD).[9] Okumura and Ito succeeded in cross-linking this PEG rotaxane via coupling reaction of CDs. This slide-ring gel has extraordinarily high performance, such as ultrahigh degree of swelling ratio and mechanical toughness, without losing its clarity.

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Table 1. Preparation Conditions and Sample Codes

sample code	f [%]	C_X [wt %]
CX0	15	0
CX1		1
CX2		2
CX3		3
CX4		4
CX5		5
FR13s	13	0
FR14s	14	0
FR15s	15	0
FR19s	19	0
FR13g	13	1.4
FR14g	14	2.7
FR15g	15	4
FR19g	19	5.7

In this paper, we investigate the structure of the slide-ring gel in terms of small-angle neutron scattering. Particularly, we focus our attention on elucidation of the roles of solvents in ruling the structure of gels. To fulfill this objective, we chose and compared dimethyl sulfoxide and NaOD aqueous solutions.

Experimental Section

Preparation of Slide-Ring Gels. *Polyrotaxane*: Poly(ethylene glycol) (PEG) and α-cyclodextrin (α-CD) were dissolved in water at 80 °C and kept at 5 °C overnight to yield a white paste. The paste was dried, followed by addition of an excess of 2,4-dinitrofluorobenzene together with dimethylformamide. 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.

Gelation in NaOD: The polyrotaxane was dissolved in a 1 N NaOD deuterium oxide solution (99.9% deuteration) ($NaOD_{aq}$) at 5 °C. Cyanuric chloride, dissolved in 1 N $NaOD_{aq}$, was mixed with the solution to initiate the cross-linking reaction. After 3 h at room temperature, we got a transparent yellow polyrotaxane gel, i.e., slide-ring gel.

Gelation in d-DMSO: Similar to the NaOD system, slide-ring gels were also prepared in deuterated dimethyl sulfoxide (99.9% deuteration) (d-DMSO), where cyanuric chloride was used as cross-linker. The cross-linker concentration, C_X, was varied from 0 to 5 wt % with respect to the polyrotaxane solution.

The Filling Ratio (f) Determination: *f*, 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 stoichiometrically a CD molecule can be included per two PEG monomer units (i.e., $f = 100\%$).

Two series of gels have been prepared in order to investigate C_X dependence (CX# series) and *f* dependence (FR# series). The characteristics of the slide-ring gels are listed in Table 1. The dummy numbers # indicate the value of C_X in wt % for the CX series and *f* in wt % for the FR series. The subscript s and g indicate the sol and gel, respectively.

Small-Angle Neutron Scattering. Small-angle neutron scattering (SANS) experiments were carried out at the SANS-U spectrometer at the Institute for Solid State Physics, University of Tokyo, Tokai, Japan. The two-dimensional detector (64 × 64 cm^2) was placed at 2 and 8 m from the sample. The incident wavelength was 7.0 Å. The samples in 2 mm quartz cell were irradiated at room temperature. The scattered intensity was circularly averaged and rescaled to the absolute intensity with a polyethylene (Lupolen) secondary standard, which was calibrated with the incoherent scattering from vanadium. Note that the polyethylene did not show any *q* dependence in the range of $0.006 \approx q \approx 0.3$ Å^{-1}, where *q* is the magnitude of the scattering vector. The incoherent scattering intensity, of the order of 0.014 cm^{-1} for 5% polyrotaxane DMSO solution, was taken into account for the analyses.

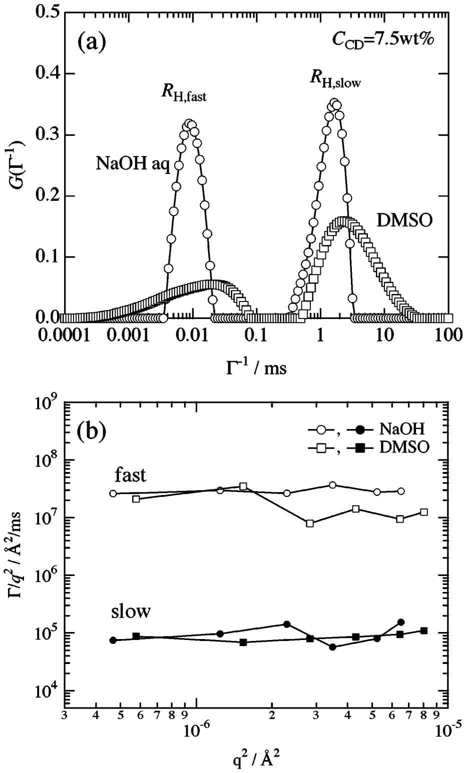

Figure 2. (a) Time distribution functions, $G(\Gamma)$, for α-cyclodextrin (CD) in $NaOH_{aq}$ (circles) and in DMSO (squares) at 90°. (b) Γ/q^2 vs q^2 plots for the fast and slow modes of CD solutions in $NaOH_{aq}$ (circles) and in DMSO (squares).

Dynamic Light Scattering (DLS). DLS experiments were carried out on a static/dynamic compact goniometer (SLS/DLS-5000), ALV, Langen Germany. A He−Ne laser with 22 mW (wavelength $\lambda = 632.8$ nm) was used as the incident beam. Time−intensity correlation functions, $g^{(2)}(\tau)$, were measured for CD solutions, filtered with 0.45 μm Millpore filter, at 25 °C for 30 s, followed by CONTIN analysis in order to obtain the decay rate distribution function, $G(\Gamma)$.

Results and Discussion

Dynamics of CDs in Solutions. DLS measurements were carried out in order to characterize CDs in $NaOH_{aq}$ and in DMSO. The CD concentration, C_{CD}, was 7.5 wt % in both cases. Figure 2a shows the characteristic decay time distribution functions observed at 90°, $G(\Gamma)$, where Γ is the characteristic decay rate. There are two peaks (modes) in $G(\Gamma)$ for both $NaOH_{aq}$ and DMSO solvents. To examine the origin of these modes, a *q*-dependent DLS measurement was also carried out. In Figure 2b were plotted Γ/q^2 vs q^2 for both the fast and slow modes. As shown in the figure, the plots are more or less flat, indicating that both modes for $NaOD_{aq}$ are diffusive. On the basis of this finding, we discuss the diffusion coefficient, *D*, estimated from the peak position of $G(\Gamma)$ via the relation of $D = \Gamma/q^2$. The hydrodynamic radius, R_H, of the diffusing objects can be estimated by

$$R_H = \frac{k_B T}{6\pi\eta D} \tag{1}$$

where k_B is the Boltzmann constant, *T* is the absolute temperature, and η is the solvent viscosity. The values of R_H for the first and slow modes are estimated to be

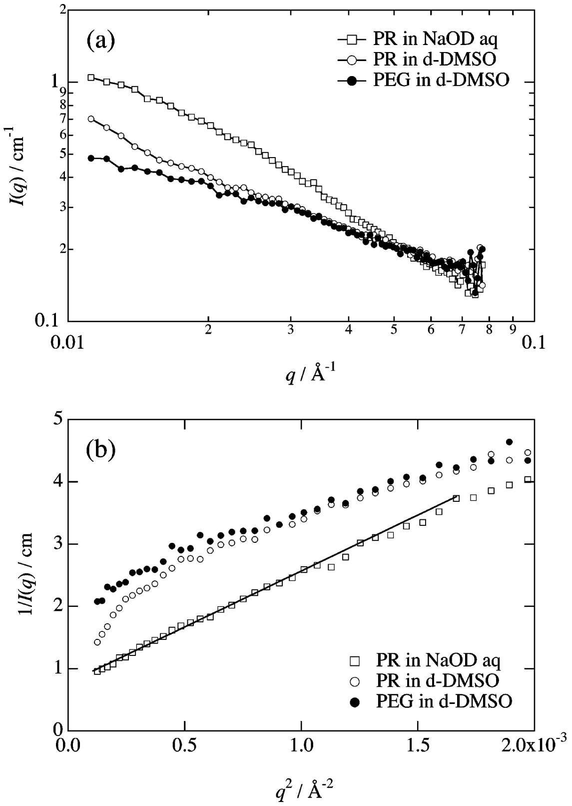

Figure 3. Scattering functions, $I(q)$, for poly(ethylene glycol) (PEG) and polyrotaxane (PR) in $NaOD_{aq}$ and in d-DMSO: (a) log−log plot and (b) OZ plot. The solid line shows the fitting result with eq 2.

1.0 and 120 nm, respectively. Since the sizes of CD molecule are 0.67 nm thick and 0.45 nm in diameter, the first mode is assigned to the translational motion of CD molecules and the slow mode is to CD aggregates. Note that the $G(\Gamma)$s are quite different between $NaOH_{aq}$ and DMSO. The peak widths are wider in DMSO than in $NaOH_{aq}$. This suggests that CD molecules in DMSO have a larger tendency of aggregation than in NaOH. The reason for this tendency is due to the fact that the hydroxyl groups of CD are ionized under a strong base, resulting in Coulombic repulsion between adjacent CDs in the polyrotaxane.

The concentration dependence of $R_{H,fast}$ was also investigated for both cases. $R_{H,fast}$ was almost constant at 1.0 nm, irrespective of the kind of solvent as it should be for the single molecular size. On the other hand, the $R_{H,slow}$ is an increasing function of C_{CD}, indicating progressive aggregation with increasing C_{CD}. Not only aggregation of CDs along a PEG chain but also that among polyrotaxane chains are highly anticipated because hydroxyl groups on polyrotaxane molecules in DMSO easily form hydrogen bonding to each other. On the other hand, the hydroxyl groups are dissociated in $NaOH_{aq}$ and are highly repelled to each other because of the electrostatic repulsion. This may be why $G(\Gamma)$ of the slow mode for $NaOH_{aq}$ in Figure 2a is much sharper than for DMSO.

Structure Factors of Pregel Solutions. Figure 3a shows the SANS intensity functions, $I(q)$, of (i) PEG, (ii) polyrotaxane (PR) in d-DMSO, and (iii) PR in $NaOD_{aq}$ solutions. The filling ratio, f, of PR was kept constant to be 15%. All of $I(q)$s are monotonic decreasing functions of q. However, the $I(q)$ of PEG at low q-region increases by addition of CD to a PEG and behaves more or less as $I(q) \sim q^{-1}$ (PR in DMSO). $I(q)$ for PR in $NaOD_{aq}$ has an even stronger q dependence with the slope of ca. −2 at least for $q \approx 0.03$ Å^{-1}.

It is known that the scattering intensity, $I(q)$, for flexible polymer solutions in semidilute solutions can be described by a Lorentz type function, i.e., Ornstein−Zernike (OZ)[10] equation given by

$$I(q) = \frac{I(0)}{1 + q^2\xi^2} \tag{2}$$

where ξ is the correlation length. Figure 3b shows the OZ plots for the solutions shown in Figure 3a. It is noteworthy that $I(q)$ for PR in $NaOD_{aq}$ can be exclusively fitted with an OZ equation as shown with the solid line. The evaluated ξ is 48.2 Å. Although PR chains in $NaOD_{aq}$ are highly ionized, but the electrostatic interactions are strongly shielded because of strong base. This is why the PR chains recover a Gaussian chain behavior, which is described by eq 2. On the other hand, the OZ plots for the PEG chains and PR in d-DMSO do not fit eq 2, meaning that the scattering exponent is less than 2 as already shown in Figure 3a. Note that $I(q)$ of PR in d-DMSO was very different from that in $NaOD_{aq}$. This difference is related to the degree of dispersion of CD molecules along a PEG chain. As already pointed out, a CD molecule has 18 hydroxyl groups on its surface, leading to aggregation of CD molecules. In d-DMSO, therefore, CD molecules on a PEG chain were assembled on a line by forming hydrogen bonds between adjacent CD molecules. Namely, CD molecules are one-dimensionally stuck along a PEG chain, resulting in an increase in the rigidity of the PEG chain. This is why PEG chains behave as a rodlike scattering object in d-DMSO, leading to $I(q) \sim q^{-1}$. In $NaOD_{aq}$, on the other hand, dissociation of hydroxyl groups of CDs prevents an assembly of CDs due to repulsion of electrostatic interaction. Therefore, the mobility of CD in NaOD would be higher than that in DMSO.

***$I(q)$* of SR Gels in $NaOD_{aq}$.** Figure 4a shows cross-linker concentration dependence of $I(q)$s for PRs in $NaOD_{aq}$. The f was fixed at 15%. The gelation concentration, C_{gel}, was determined to be 3% by flow behavior observation. It is surprisingly enough that $I(q)$s decreased with increasing C_X for low C_Xs and then increases with C_X for high C_Xs. The lowering in $I(q)$ with C_X is an opposite tendency of the conventional chemical gels.[11,12] In general, $I(q)$ increases with increasing C_X. However, $I(q)$ for PRs in $NaOD_{aq}$ increased with increasing C_X above C_{gel}. Figure 4b shows OZ plots for PRs in $NaOD_{aq}$. As shown in the figure, each of the $1/I(q)$ plot exhibits a straight line, indicating that the polymer chains behave as flexible chains in the semidilute regime. Static light scattering (SLS) experiments were also carried out to investigate the $I(q)$ behavior at lower q range. $I(q)$s were monotonic decreasing functions with q in the range of $0.0006 < q < 0.002$ Å^{-1}. Though $I(q)$s seem to be extrapolated to the scattering intensity obtained by SANS, we did not construct a mater curve due to the missing q range ($0.002 < q < 0.01$ Å^{-1}).

Figure 5 shows $I(0)$ and ξ evaluated from the OZ plots in Figure 3b. Interestingly, both $I(0)$ and ξ have a minimum as a function of C_X. This minimum corresponds to C_{gel}. Below C_{gel}, finite clusters are made owing to introduction of cross-links. The decrease in ξ seems to be a good indication of the presence of sliding cross-

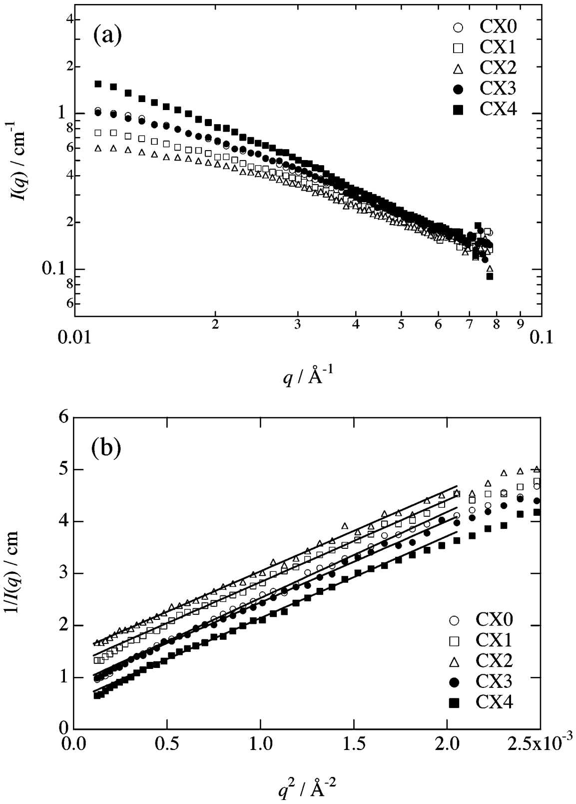

Figure 4. Scattering functions for the CX series of the slide-ring gels in $NaOD_{aq}$: (a) log–log plot and (b) OZ plot. The solid lines show the fitting result with eq 2.

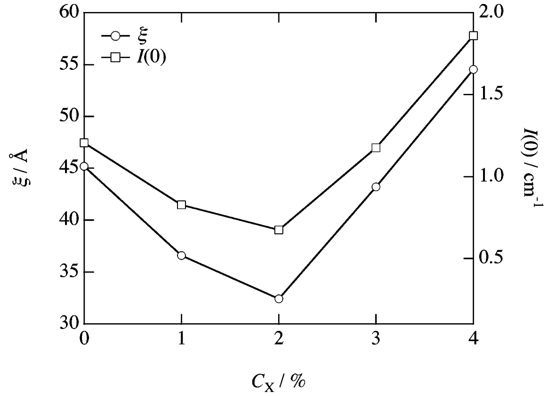

Figure 5. C_X dependence of $I(0)$ and ξ in $NaOD_{aq}$.

links. In general, an introduction of cross-links leads to an increase in the scattering intensity at low-q region due to an increase in frozen heterogeneities.[3,13] However, concentration fluctuations of PR solutions are suppressed by introduction of sliding cross-links even lower than the case of their mother polymer solution because cross-linking has an effect to suppress concentration fluctuations. As a result, ξ decreases. Further introduction of cross-links, however, leads to an increase in heterogeneities and an increase in the scattering intensity and ξ. Concurrently, the spatial inhomogeneities are suppressed by increasing C_X, leading to a decrease in $I(0)$. After C_{gel}, both $I(0)$ and ξ increased with increasing C_X as is the case of conventional chemical gels. It is noteworthy that $I(0)$ is well described with an OZ function even for the gel regime. In the case of conventional chemical gels, an excess scattering appears due to emergence of spatial frozen inhomogeneities.[14] Therefore, the applicability of the OZ equation may be one of the unique features of SR gels. This strange behavior of scattering function is attributed to unique arrangement of CDs on PEG chains. In $NaOD_{aq}$, the hydroxyl groups on CDs have negative charges, generating a repulsive electrostatic interaction to separate CD molecules as far as possible. As a result, the system becomes uniform, and $I(0)$ decreases for $C_X < C_{gel}$, whereas above C_{gel}, $I(0)$ increases with increasing C_X.

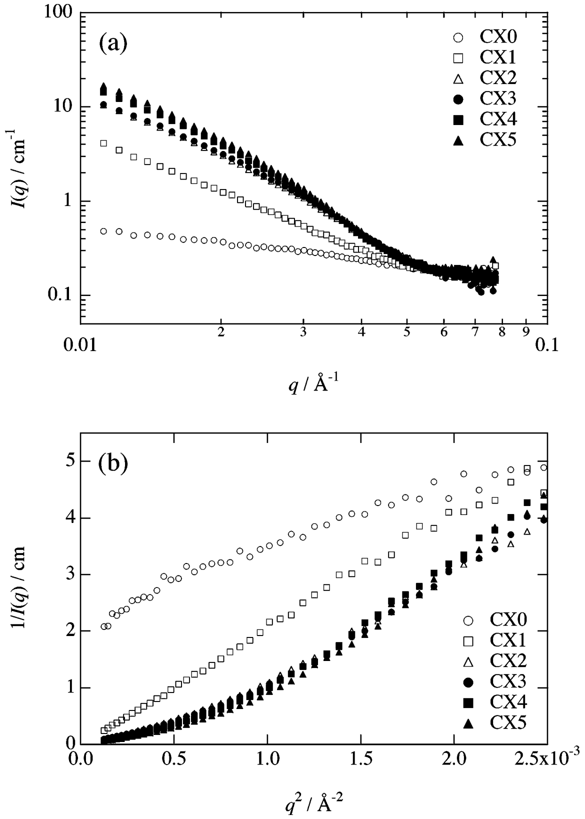

Figure 6. Scattering functions for the CX series of the slide-ring gels in d-DMSO: (a) log–log plot and (b) OZ plot.

Structure Factors of SR Gels in d-DMSO. Figure 6a shows a C_X dependence of $I(q)$ for the CX series in d-DMSO. The f was fixed at 15%, and the value of C_{gel} was 3%. Note that this value is the same as those prepared in $NaOD_{aq}$, indicating that the cross-linker concentration to form a gel is independent of the solvent. However, $I(q)$ in d-DMSO increased with increasing C_X in contrast to that in NaOD. This behavior is similar to the conventional chemical gels. In particular, $I(q)$ increases strongly up to C_{gel}. Above C_{gel}, the increase in $I(q)$ is suppressed, resulting in a gradual increase. Figure 6b shows OZ plots for the $I(q)$s. None of the OZs plots give a straight line, suggesting a failure of the OZ analysis. This means that PR solutions and gels (i.e., SR gel) in DMSO are far from a homogeneous system. As already discussed, CD molecules on PEG chains prefer to aggregate in DMSO. This may result in a rodlike conformation of PR chains. This conjecture is supported by the fact that $I(q)$ in the high-q region is proportional to q^{-1}.

Now, let us introduced a new type of scattering function for the polymer gels on the basis of the findings disclosed above. The new scattering function has an inhomogeneous component as well as a rodlike behavior.

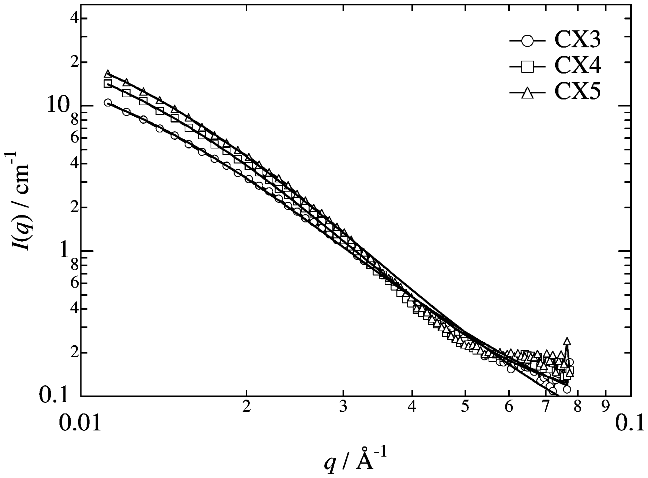

Figure 7. Scattering functions for the CX series of the slide-ring gels in d-DMSO. The solid lines are fits with a squared Lorentz function and a rod function (eq 3 in the text).

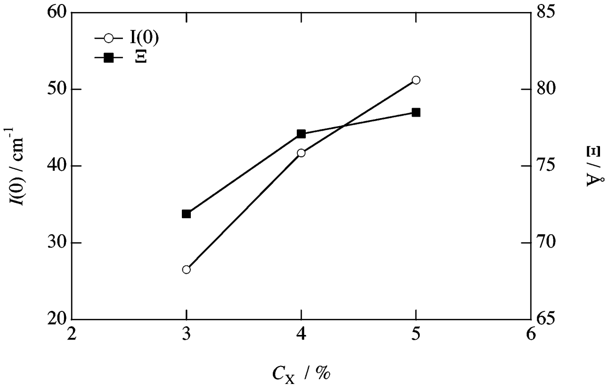

Figure 8. C_X dependence of $I(0)$ and ξ in d-DMSO.

Hence, it is given by

$$I(q) = \frac{I(0)}{(1 + \Xi^2 q^2)^2} + I(0)_R q^{-1} \tag{3}$$

where Ξ is the correlation length corresponding to the spatial inhomogeneities and $I(0)$ is the zero-q scattering intensity. The first term of the right-hand side of eq 3 shows the spatial inhomogeneities of the gels or two-phase separated structure.[15] This term is identical to the Debye–Bueche equation.[16] The second term describes rodlike chains as a local structure of gels.

Figure 7 shows the fitting results for CX3–CX5. This unique function, e.g., eq 3, exclusively enabled us to fit the observed scattering functions. The scattering intensity of the CX series for $q \approx 0.06$ Å^{-1} may suggest presence of aggregates which cannot be represented by eq 3. We believe, however, this model is still valid for lower q range.

Figure 8 shows the C_X dependence of Ξ and $I(0)$. As expected, both I (0) and Ξ increase with increasing the cross-link concentration, indicating an increase in inhomogeneities with increasing C_X. Note that this behavior is quite different from that in the case of NaOD (see Figures 4 and 5).

Filling Ratio Dependence. Figure 9 shows the filling ratio, f, dependence of $I(q)$ for (a) PR solutions and (b) SR gel (i.e., PR gels) in d-DMSO. The f was varied from 13% to 19% by keeping the ratio of CD to cross-linker concentrations. In the case of the solutions, $I(q)$s seem to be independent of f and are roughly scaled as $I(q) \sim q^{-1}$. This means that PRs behave as rodlike chains in d-DMSO. In the case of SR gel, on the other hand, $I(0)$s increase with increasing f. As compared with the PR solutions, $I(0)$s increased by introduction of mobile cross-links. In particular, $I(0)$s increase remarkably in the small q region as f increases.

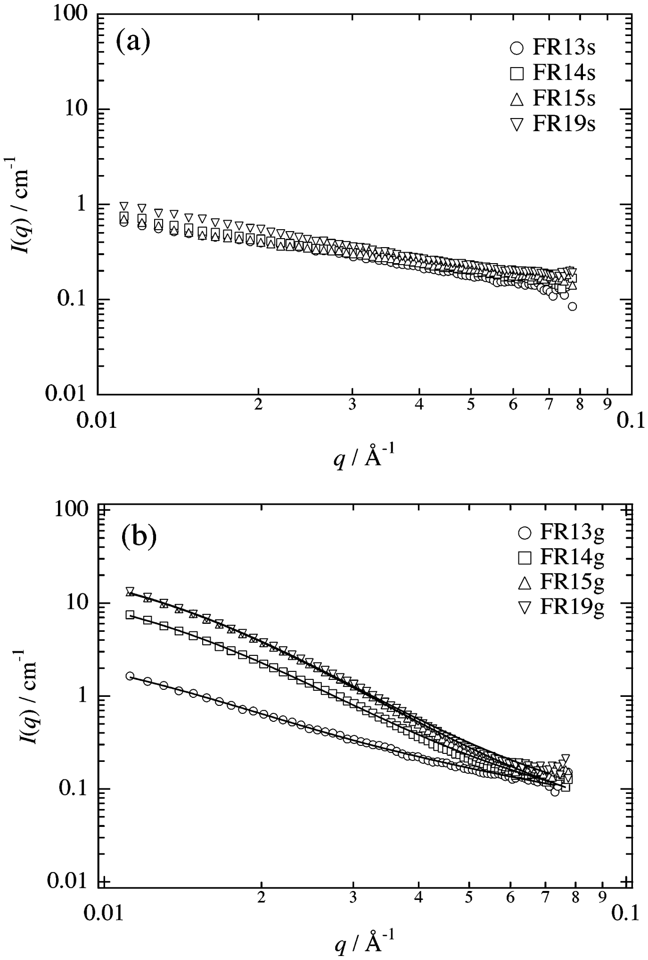

Figure 9. Scattering functions for the FR series of the slide-ring gels in d-DMSO: (a) sol and (b) gel. The solid lines are fits with a squared Lorentz function and a rod function (eq 3 in the text).

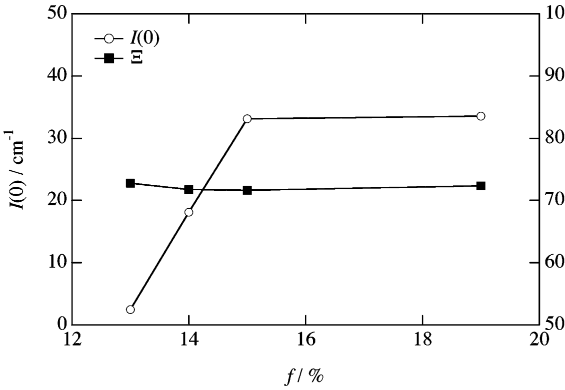

Figure 10. f dependence of $I(0)$ and ξ in d-DMSO.

Similar to the case of C_X dependence for SR gel in CX series, $I(q)$s for the SR gel in FR series were successfully fitted with eq 3 as shown in the solid lines in Figure 9b. Figure 10 shows the fitting parameters. Interestingly, Ξs are independent of f. On the other hand, $I(0)$ exhibits a jumpwise increase between $f = 13$

and 14% of f and levels off for $f \approx 14\%$. This indicates that a cross-linking saturation[13] takes place depending on the filling ratio f. In other words, the number of CD molecules on a PEG chain rules the degree of cross-linking, and cross-linking saturation takes place at $f \approx 15\%$ and $C_X \approx 5\%$. The presence of this ceiling concentrations may be due to steric hindrance and rigidity of the polyrotaxane chains which prevent from further cross-linking.

Conclusion

The DLS and SANS experiments were carried out to elucidate the dynamics and microstructure of slide-ring gels (SR gel) in NaOD aqueous solutions ($NaOD_{aq}$) and in deuterated dimethyl sulfoxide (d-DMSO). The slide-ring gels were successfully prepared by coupling reaction of α-cyclodextrin molecules on polyrotaxane (PR) chains made of poly(ethylene glycol) (PEG) and α-cyclodextrin (CD). The DLS studies on CD and SANS on PEG, PR, and SR gel in the two different solvents disclosed the following facts. (1) The mobile cross-links behave like a pulley on the polymer chain. The pulley effects of the slide-ring gels and $I(q)$s differ greatly from each other between DMSO and $NaOD_{aq}$. (2) Rodlike conformation of the PR chains were deduced in d-DMSO because of $I(q) \sim q^{-1}$ in the high-q region. However, $I(q)$s in NaOD behave as Gaussian chains. (3) $I(q)$s of gels in d-DMSO were stronger than that in $NaOD_{aq}$. This means that the spatial inhomogeneities in DMSO were larger than that in $NaOD_{aq}$. SR gels suppress spatial inhomogeneities by adjusting the location of slide-ring cross-links so as to minimize the elastic free energy of the network. (4) CD molecules in $NaOD_{aq}$ are distributed due to repulsion of the electrostatic interaction between hydroxyl groups of CD molecules. Since the mobility of CD molecules is high, the spatial inhomogeneities can be effectively reduced. On the other hand, CD molecules in DMSO easily self-assemble by hydrogen bonding. This results in that the mobility of CD molecules are highly suppressed.

These experimental findings indicate that the degree of spatial inhomogeneities of SR gel in DMSO is larger than that in $NaOD_{aq}$. From these results, it is concluded that the pulley effect of SR gel in $NaOD_{aq}$ is more effective than that in DMSO. These differences in $I(q)$ are ascribed to the difference in the stacking behavior of CD molecules on PEG chains in PR. These results indicate the mobility of the slide-rings and the conformation of the PR chains in the SR gel strongly depend on the choice of solvent. SR gels in $NaOD_{aq}$ seem to be a more suitable system than in DMSO for sliding capability of CD molecules along PEG chains.

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References and Notes

(1) Osada, Y., Kajiwara, K., Eds.; *Gel Handbook*; Academic Press: New York, 2001.
(2) Guenet, J. M. *Thermoreversible Gelation of Polymers and Biopolymers*; Academic Press: New York, 1992.
(3) Shibayama, M. *Macromol. Chem. Phys.* **1998**, *199*, 1.
(4) Ngai, T.; Wu, C.; Chen, Y. *Macromolecules* **2004**, *37*, 987.
(5) Takata, S.; Suzuki, K.; Shibayama, M.; Norisuye, T. *Polymer* **2002**, *43*, 3101.
(6) Norisuye, T.; Masui, N.; Kida, Y.; Shibayama, M.; Ikuta, D.; Kokufuta, E.; Ito, S.; Panyukov, S. *Polymer* **2002**, *43*, 5289.
(7) Norisuye, T.; Kida, Y.; Masui, N.; Tran-Cong-Miyata, Q.; Maekawa, Y.; Yoshida, M.; Shibayama, M. *Macromolecules* **2003**, *36*, 6202.
(8) Okumura, Y.; Ito, K. *Adv. Mater.* **2001**, *13*, 485.
(9) Harada, A.; Kamachi, M. *Macromolecules* **1990**, *23*, 2821.
(10) Stanley, H. E. *Introduction to Phase Transition and Critical Phenomena*; Oxford University Press: New York, 1971.
(11) Mallam, S.; Horkay, F.; Hecht, A. M.; Geissler, E. *Macromolecules* **1989**, *22*, 3356.
(12) Shibayama, M.; Norisuye, T.; Nomura, S. *Macromolecules* **1996**, *29*, 8746.
(13) Panyukov, S.; Rabin, Y. *Phys. Rep.* **1996**, *269*, 1.
(14) Panyukov, S.; Rabin, Y. *Macromolecules* **1996**, *29*, 7960.
(15) Onuki, A. *J. Phys. II* **1992**, *2*, 45.
(16) Debye, P.; Bueche, A. M. *J. Appl. Phys.* **1949**, *20*, 518.

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