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Sliding mode of cyclodextrin in polyrotaxane and slide-ring gel

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Abstract

The sliding modes of cyclic molecules in polyrotaxane and of cross-linking junctions in topological gel or slide-ring gel were investigated by quasi-elastic light scattering. We found that a polyrotaxane sparsely including α -cyclodextrin showed the sliding mode in solution other than the self- and cooperative-diffusion modes whereas the sliding mode was not observed in a polyrotaxane densely including α -cyclodextrin. After gelation of the sparse polyrotaxane, the self-diffusion mode of the polyrotaxane disappeared but the sliding mode was still observed. This indicated that the figure-of-eight cross-links in the slide-ring gel slid in the polymer network, passing through the polymer chains.

1. Introduction

All gels are classified into two groups from the viewpoint of network junction points: physical and chemical gels [1]. Physical gels have noncovalent cross-links, such as hydrogen bonding, and hydrophobic interaction. On the other hand, chemical gels, with covalent cross-links, are more stable than physical gels, and therefore have been applied in many uses, such as soft contact lenses. However, a chemical gel generally has large inhomogeneous structure due to the gelation process [2], which considerably reduces the mechanical strength of the chemical gel. In the chemical gel, long polymer chains are divided into short pieces with different lengths by fixed cross-links. As a result, the tensile stress concentrates on the shortest chains and the chemical gel easily breaks down.

We have recently developed a novel kind of gel that is different from physical and chemical gels: a topological gel or slide-ring gel, based on supramolecular architecture with

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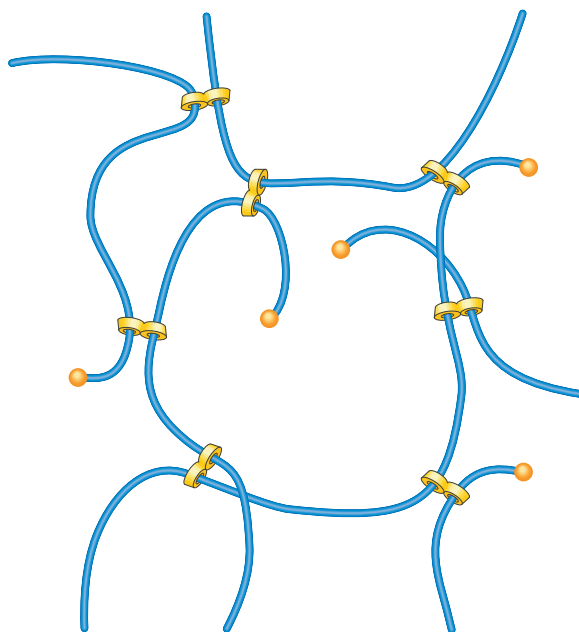


Figure 1. A schematic diagram of the slide-ring gel. Polyrotaxanes are cross-linked through figure-of-eight junctions.

(This figure is in colour only in the electronic version)

topological characteristics (figure 1) [3]. A typical example of the topological architecture is the polyrotaxane or molecular necklace in which α -cyclodextrins (α -CDs) are threaded on a poly(ethylene glycol) (PEG) chain and are trapped by capping the chain with bulky end groups [4]. We chemically cross-linked α -CDs contained in polyrotaxanes sparsely populated with α -CD to form the slide-ring gel. In the slide-ring gel, the polymer chains with bulky end groups are neither covalently cross-linked like chemical gels nor attractively interacted like physical gels, but are topologically interlocked by figure-of-eight cross-links. Therefore, the figure-of-eight cross-links can pass through the polymer chains freely to equalize the ‘tension’ of the threading polymer chains, just like pulleys. Incidentally, a few physical and chemical gels with polyrotaxane architectures have been reported so far [5–7]. But the slide-ring gel is different from the other polyrotaxane gels in that it has movable cross-linking junctions in the polymer network [8].

The purpose of this study is to confirm the sliding of the figure-of-eight cross-links in the slide-ring gel by quasi-elastic light scattering (QELS). We compare two kinds of polyrotaxanes: a polyrotaxane in which a PEG chain is sparsely populated with α -CD and the other in which α -CD is densely packed. The sliding mode may be suppressed in the dense polyrotaxane. This enables us to identify the sliding mode of α -CD in the polyrotaxane. Next, we measure the quasi-elastic light scattering of the slide-ring gel to determine whether the figure-of-eight cross-links really slide in the polymer network or not.

2. Materials and methods

Monodisperse PEG ($M_w = 35\,000$, Fluka) (50 g) was dried in vacuum at 50 °C for 2 h and was dissolved in dehydrated tetrahydrofuran (Wako Pure Chemical Industries Ltd) (200 ml) at

60 °C. Then *n,n'*-carbonyldiimidazole (Nacalai Tesque) (2.0 g) was dissolved in the solution. After the solution had been kept at 50 °C for 18 h, ethylenediamine (6.0 ml) was added to it and reacted at 50 °C for 2 h. After adding ethanol (200 ml), the reaction mixture was cooled in a refrigerator (5 °C) to precipitate a white paste, which was repeatedly washed with ethanol. The white paste was dissolved at 60 °C in ethanol (400 ml) and was precipitated at 5 °C. The product was washed in a suction funnel with ethanol (1 l) and dried in vacuum at 30 °C to give PEG-BA ($M_w = 35\,000$).

The PEG-BA (3.6 g) and α -CD (Nacalai Tesque) (14.4 g) were respectively dissolved in water (60 ml) at 80 °C, and then both solutions were mixed at 80 °C and kept at 5 °C overnight to yield the white paste of the inclusion complex. We dried the paste in vacuum at room temperature, added an excess 2,4-dinitrofluorobenzene (Wako Pure Chemical Industries Ltd) (9.6 ml) together with dimethylformamide (Wako Pure Chemical Industries Ltd) (40 ml) and stirred the mixture in a nitrogen atmosphere at room temperature overnight. The reaction mixture was washed with dimethylformamide (200 ml) three times, dissolved in dimethyl sulfoxide (Wako Pure Chemical Industries Ltd) (160 ml), and then precipitated from 0.1% sodium chloride aqueous solution (2800 ml) twice to give a yellow product. The product was collected, washed with water and methanol (three times, respectively), and dried to produce the polyrotaxane PR-A (6 g). The polyrotaxane PR-B was synthesized from monodisperse PEG-BA ($M_w = 3300$, Aldrich Chemical Co. Ltd) according to Harada's method [4].

The filling ratio (FR) of α -CD in polyrotaxane was calculated by comparing the summation of peak integrations from 6 to 4 ppm (C-2 OH, C-3 OH, C-6 OH and C-1 H, all belonging to α -CD) and integrations from 4 to 2.6 ppm (the other H peaks including H in the α -CD and PEG chain). The FRs of PR-A and PR-B were determined to be 27% and 60%, respectively.

The QELS experiments were carried out with a static/dynamic compact goniometer (ALV-6000, Langen Germany) at a fixed angle of 90°. A He-Ne laser with 22 mW (wavelength 632.8 nm) was used as the incident beam and the scattered angle was fixed at 90°. The PR-A and PR-B were dissolved in 1N NaOH aqueous solution at a concentration of 10 wt% and filtered through a 0.45 μm micropore Teflon filter. The time-intensity correlation functions were measured at 300 °C for 60 s, followed by CONTIN analysis [9] in order to obtain the decay rate distribution function, $G(\Gamma)$. The PR-A (150 mg) was dissolved in 1N NaOH (0.75 ml) at 5 °C for the gelation measurement. Cyanuric chloride (Tokyo Kasei Co.) (53 mg), dissolved in 1N NaOH (0.75 ml), was added to the solution to initiate the cross-linking reaction, and the solution was filtered through a 0.45 μm micropore Teflon filter. The time-intensity correlation functions were measured at 20 °C for 60 s at intervals of about 1.8 h, followed by CONTIN analysis in order to obtain the decay rate distribution function, $G(\Gamma)$.

3. Results and discussion

Figure 2 shows $G(\Gamma)$ for the sparse polyrotaxane PR-A in NaOH aqueous solution. The semi-dilute solution of linear polymer chains in general exhibits the self- and cooperative diffusion modes [10, 11]. However, three diffusion modes are observed in figure 2. On the other hand, only two modes are detected for the dense polyrotaxane PR-B, as shown in figure 3. To determine the diffusion modes, we measured the dependence of the characteristic decay time on the concentration of polyrotaxane. As shown in figure 4, three modes show contrast concentration dependence: the fastest mode increases with concentration but the slowest one decreases, while the other mode is nearly independent of the concentration. From the concentration dependence, the fastest and slowest modes should be identified as the cooperative and self-diffusion ones, respectively. Accordingly, we can conclude that the other mode observed only in the sparse polyrotaxane is attributed to the sliding mode of α -CD

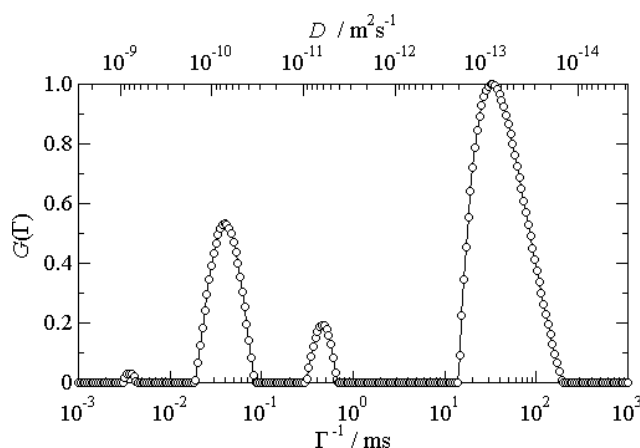


Figure 2. The decay rate distribution function $G(\Gamma)$ of the PR-A (sparse polyrotaxane) solution. Three peaks were observed.

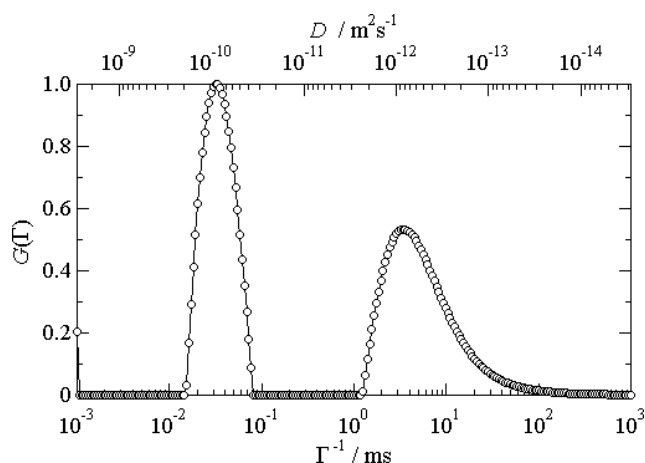


Figure 3. The decay rate distribution function $G(\Gamma)$ of the PR-B (dense polyrotaxane) solution. Two peaks were observed.

on the PEG chain. In the dense polyrotaxane, α -CD is probably too closely packed to move along a chain and hence to cause the sliding mode.

Figure 5 shows $G(\Gamma)$ for the gelation process of the sparse polyrotaxane. The gelation threshold was after 70 min. Before gelation, three peaks are observed, as shown in figure 2. After gelation, the slowest peak disappears, which clearly indicates that this peak corresponds to the self-diffusion mode. However, the middle peak does exist after gelation. This demonstrates that figure-of-eight cross-links of the slide-ring gel move in the polymer network. On the other hand, the correlation times of the cooperative diffusion mode are almost constant during gelation. The cooperative diffusion mode reflects the correlation length of polyrotaxanes; consequently, the experimental results indicate that the correlation length is not affected by the gelation process.

Let us discuss the conformation and concentration regime of PR-A and PR-B in this study. In a previous paper, we demonstrated by small-angle neutron scattering that a polyrotaxane with PEG of $M_w = 10\,000$ and FR = 13–19% has a rod-like conformation in the scale of

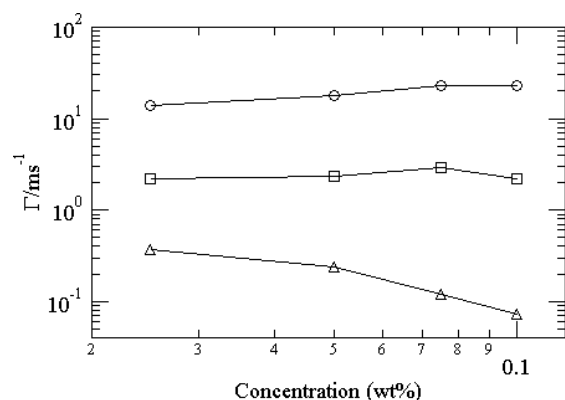


Figure 4. The concentration dependence of the three diffusion modes.

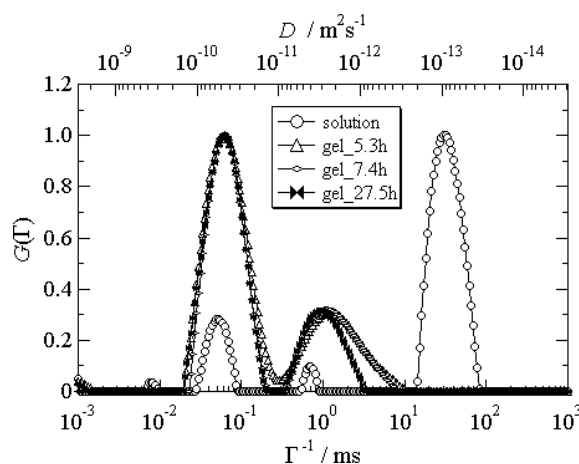


Figure 5. The decay rate distribution function $G(\Gamma)$ of the PR-A (sparse polyrotaxane) solution in the gelation time: gel_5.3h, gel_7.4h and gel_27.5h represent 5.3 h, 7.4 h and 27.5 h elapsed after the gelation, respectively. The slowest mode disappeared but the other modes were still observed.

1–10 nm in dimethyl sulfoxide (DMSO) whereas it has a flexible conformation in NaOH [12]. This is mainly because α -CD molecules in a polyrotaxane in DMSO are one-dimensionally stuck along a PEG chain by hydrogen bonding between adjacent α -CDs and thereby give a polyrotaxane local stiffness. Since an α -CD molecule includes two monomer units of PEG, the inclusion complex formation of α -CD and PEG inherently stretches the PEG chain in polyrotaxane. The polyrotaxanes used in this study have larger FRs (27% for PR-A and 60% for PR-B) and shorter PEG length ($M_w = 35\,000$ for PR-A and 3350 for PR-B) than those in the previous paper; accordingly PR-B and PR-A are likely to have rod-like and semi-flexible conformations, respectively, even in NaOH.

The chain lengths L of PR-A and PR-B are determined to be 290 and 28 nm from the effective monomer length ($b = 0.35$ nm) [13] of the PEG chain in PR-A and PR-B, respectively. Assuming that PR-B has a rod-like conformation, the polymer concentration $c_p = 3.9$ ml $^{-1}$ gives $c_p L^3 \approx 51$, which indicates that the polyrotaxanes are highly entangled with each other, i.e., the semi-dilute regime. On the other hand, even if PR-A ($c_p = 0.7$ mM l $^{-1}$) has the coiled conformation, the radius of gyration $R = 20$ nm estimated from $R = bN^{3/5}$ gives $c_p R^3 \approx 3.4$, also indicating the semi-dilute regime, where N is the degree of polymerization. Actually PR-A has a more stretched conformation as mentioned above; hence the PR-A solution in this study should belong to the semi-dilute regime. This is consistent with the experimental results that both the PR-A and PR-B solutions showed the cooperative diffusion modes.

The correlation times of the cooperative modes in PR-A and PR-B are close to each other ($\Gamma^{-1} = 32 \mu\text{s}$ for PR-A, $\Gamma^{-1} = 55 \mu\text{s}$ for PR-B) although the polymer length of PR-A is over ten times longer than that of PR-B. From them, the correlation lengths ξ are given as $\xi = 3.2 \text{ nm}$ for PR-A and $\xi = 5.4 \text{ nm}$ for PR-B by

$$D = \frac{\Gamma}{q^2} = \frac{k_{\text{B}}T}{6\pi\eta\xi}. \quad (1)$$

where D is the diffusion constant, q the magnitude of the scattering vector, η the solvent viscosity, and $k_{\text{B}}T$ the thermal energy. The correlation length of rod-like or semi-flexible polymer chains in the semi-dilute solution corresponds to the average distance among polymer chains, which is dependent only on the monomer concentration and independent of the polymer chain length L . Then the average distance d is roughly estimated as $d = 2.9 \text{ nm}$ for PR-A and $d = 3.9 \text{ nm}$ for PR-B from

$$c_{\text{p}}d^2L \sim 1. \quad (2)$$

These values are almost equal to the correlation length ξ for PR-A, and close to ξ for PR-B. This strongly supports the validity of the picture that the rod-like or semi-flexible polyrotaxanes are highly entangled with each other in the semi-dilute solution.

The diffusion constant of α -CD in polyrotaxane is determined to be $6.2 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ from the correlation time $\Gamma^{-1} = 0.46 \text{ ms}$ of the sliding mode with equation (1). We measured the diffusion constant of the free α -CD and obtained the value of $3.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. This corresponds to the hydrodynamic radius of 0.92 nm , almost the same size as α -CD. Consequently, the diffusion constant of α -CD in polyrotaxane is by two orders of magnitude smaller than that of free α -CD. This suggests that the diffusion of α -CD on PEG is hindered substantially. Since the inside diameter of α -CD is quite small, only the trans form of PEG can be included into α -CD. Hence the transformation from gauche to trans is required so that the α -CD includes a PEG chain. This transformation should hinder the free diffusion of α -CD in polyrotaxane considerably.

We measured the QELS of the polyrotaxane solutions and slide-ring gel. The sparse polyrotaxane showed three diffusion modes including the sliding mode while the dense polyrotaxane exhibited only two modes: the cooperative and self diffusion modes. The sliding mode was still observed after gelation; the self-diffusion mode disappeared. The evaluation of the correlation length led to the conclusion that the rod-like or semi-flexible polyrotaxanes are highly entangled in the polyrotaxane solutions. The diffusion constant of α -CD in the sliding mode was two orders of magnitude smaller than the free diffusion, which should result from the transformation of the PEG chain.

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