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Mechanically Interlocked Structure of Polyrotaxane Investigated by Contrast Variation Small-Angle Neutron Scattering

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Advances in supramolecular chemistry have led to the development of novel polymer architectures composed of several noncovalently bonded components.[1] One of the most promising supramolecules is polyrotaxane (PR), in which cyclic molecules are threaded into a linear polymer chain.[2−6] Covering of the axial polymer chain with cyclic molecules has resulted in various applications to nanomaterials such as molecular tubes formed by the cross-linking of adjacent cyclic molecules in a single PR[7] and insulated molecular wires incorporating conductive polymers.[8] The cyclic molecules in PR are mechanically interlocked with the axial polymer, and they can slide and rotate on the chain. This additional kinetic freedom has been utilized to prepare functional nanomaterials having novel dynamical properties, such as drug delivery systems,[9] multivalent ligand systems,[10] energy transfer systems,[11] and three-dimensionally cross-linked PR networks with movable cross-links.[2,12,13] The mechanically interlocked structure of PR is responsible for its various applications to nanomaterials.

In a previous study, Shigekawa et al. analyzed the molecular structure of PR, composed of polyethylene glycol (PEG) and α-cyclodextrins (CDs),[14] placed on a substrate by scanning tunneling microscopy (STM)[15] and observed the spatial distribution and orientation of CDs in PR. The conformation of the PR in solution, which is of considerable importance in many applications, has been studied by small-angle neutron scattering (SANS).[16−19] SANS experiments on dilute solutions of polyrotaxane have shown that threading CDs in PEG changes the conformation of the polymer chain from a Gaussian to a rodlike chain. In the case of highly concentrated polyrotaxane solutions, it was reported that CDs in polyrotaxane aggregated and formed nanocylinders.[20] However, the structural information obtained in the SANS experiments is a sum of contributions of CDs and PEG composing PR, and hence, the conformation of each component has not yet been determined.

SANS with contrast variation is a powerful method for investigating the structure of multicomponent systems such as polymer aggregates formed by a diblock copolymer,[21] inorganic crystals in the presence of a polymer,[22] and polymer−clay nanocomposite hydrogels.[23] The contrast variation analysis allows us to decompose the observed scattering intensities with different contrasts into the partial scattering functions of each component. With regard to a supramolecule, which is a typical multicomponent system, contrast variation SANS is expected to yield detailed information on its structure and the structures of its components.

In this study, we investigate the detailed structure of PR in solution by using contrast variation SANS. We decompose the scattering function of PR into partial scattering functions of PEG and CD, and then determine the conformation of PEG in PR and the spatial distribution of CDs on PEG. The pair correlation of PEG and CD arising from the decomposition of the scattering function of PR will be a measure of the mechanically interlocked connection between the two components.

The scattering intensity $I(Q)$ of PR in solution can be expressed using partial scattering functions $S_{ij}(Q)$ as

$$I(Q) = \Delta\rho_C{}^2 S_{CC}(Q) + \Delta\rho_P{}^2 S_{PP}(Q) + 2\Delta\rho_C \Delta\rho_P S_{CP}(Q) \quad (1)$$

where $\Delta\rho_i$ is the difference between the scattering-length densities ρ of a component i, which is either C for CD or P for PEG, and a solvent. S_{ij} is the partial scattering function determined by the self-correlation (i = j) or cross correlation (i ≠ j) of components i and j. The physical meanings of the partial scattering functions are schematically illustrated in Figure 1. The self-terms $S_{CC}(Q)$ and $S_{PP}(Q)$ denote the static structures of CD and PEG, respectively, and the cross-term $S_{CP}(Q)$ denotes the pair correlation of CD and PEG. The three unknown partial scattering functions S_{ij} can be determined by measuring more than three scattering intensities $I(Q)$'s having different scattering contrasts.

In order to facilitate detailed SANS measurements by contrast variation, we synthesize two types of PRs with different contrasts: h-PR, composed of α-cyclodextrin (CD) and hydrogenated PEG (h-PEG), and d-PR, composed of CD and deuterated PEG (d-PEG). In order to prevent CDs going out of PEG, PEG is end-capped with adamantane. The details of the synthesis procedure have been reported elsewhere.[24] The scattering-length densities ρ of h-PEG, d-PEG, and CD are 0.65×10^{10}, 7.1×10^{10}, and 2.0×10^{10} cm^{-2}, respectively. The degree of polymerization of both h-PEG and d-PEG is 800, and the coverage of CDs on PEG is approximately 27%; here, 100% coverage is defined as a CD being placed on every two units of PEG. In this experiment, we prepared solutions of h-PR and d-PR with a volume fraction of 8% in mixtures of DMSO-d_6 and DMSO. The volume fractions of DMSO-d_6 were 1.0, 0.95, 0.90, and 0.85, and the corresponding scattering-length densities of the solvents were (5.3×10^{10}, 5.0×10^{10}, 4.7×10^{10}, and 4.5×10^{10}) cm^{-2}, respectively. The scattering functions of the eight solutions were measured by SANS. The scattering-length densities of all the components are summarized in Figure 2.

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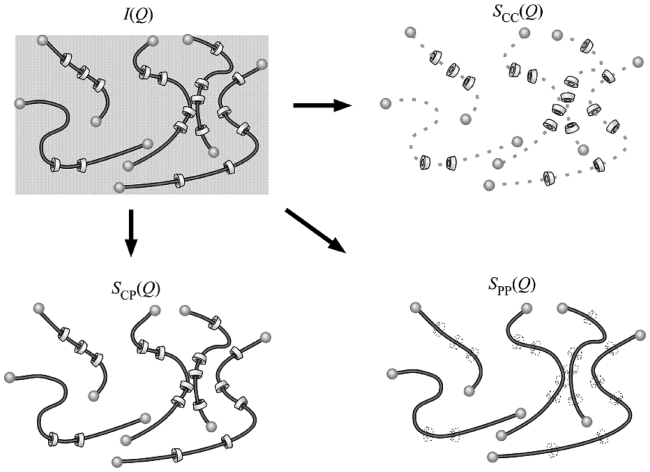

Figure 1. Schematic representations of polyrotaxane in solution showing the decomposition of scattering intensity $I(Q)$ into three partial scattering functions: self-term of PEG, $S_{PP}(Q)$; self-term of CD, $S_{CC}(Q)$; a cross-term of PEG and CD, $S_{CP}(Q)$.

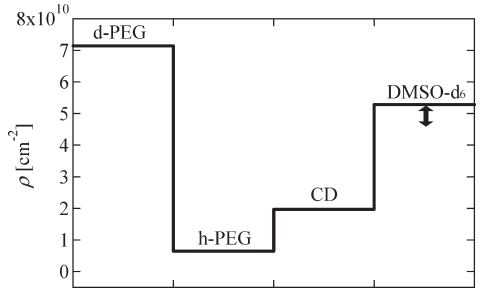

Figure 2. Scattering-length densities ρ of h-PEG, d-PEG, CD, and DMSO-d_6. The arrow indicates the range of the scattering-length density of the mixtures of DMSO-d_6 and DMSO in which the volume fractions of DMSO-d_6 are 1.0, 0.95, 0.90, and 0.85.

SANS measurements of PR solutions were performed at 298 K by using the SANS-U diffractometer of the Institute for Solid State Physics, University of Tokyo, located at the JRR-3 M research reactor of the Japan Atomic Energy Agency in Tokai, Japan.[25] The incident wavelength was 7.0 Å, and the wavelength distribution was 10%. The covered range of scattering wavenumber Q was $0.01\ \text{Å}^{-1} < Q < 0.3\ \text{Å}^{-1}$. The scattered neutrons were collected with a two-dimensional detector and then the necessary corrections were made, such as air and cell scattering subtractions. After these corrections, the scattered intensity was normalized to the absolute intensity using a standard sample with known absolute scattering intensity. The two-dimensional intensity data were circularly averaged and the incoherent scattering were subtracted.[26]

$I(Q)$'s of h-PR and d-PR obtained by the SANS measurements are shown in Figure 3. The scattering curves of d-PR are convex downward, whereas those of h-PR are convex upward. This significant difference arises due to the sign of the prefactor of $S_{CP}(Q)$. As shown in Figure 2, the scattering-length densities of the solvents are intermediate between those of h-PEG and d-PEG, and therefore, h-PEG and d-PEG have a positive and negative $\Delta\rho$, respectively. The $\Delta\rho$ determines the sign of the prefactor of $S_{CP}(Q)$ in eq 1 and the shape of $I(Q)$ profiles.

To facilitate a more quantitative discussion, the eight $I(Q)$'s having different contrasts are decomposed into partial scattering functions $S_{ij}(Q)$. The decomposed $S_{CC}(Q)$, $S_{PP}(Q)$, and $S_{CP}(Q)$ are shown in Figure 4. The self-term of CD, $S_{CC}(Q)$, is larger than the self-term of PEG, $S_{PP}(Q)$. This is because the volume fraction of CD in a PR is about two point four times as larger as that of

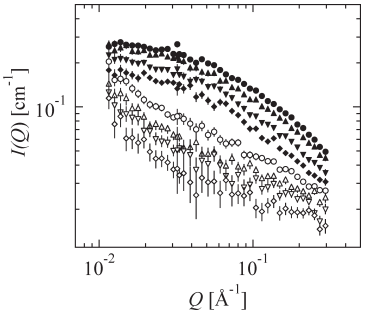

Figure 3. Scattering intensities of h-PR (solid symbols) and d-PR (open symbols) in mixtures of DMSO-d_6 and DMSO. Circles (●, ○), upward triangles (▲, △), downward triangles (▼, ▽), and diamonds (♦, ◊) correspond to $\phi_{DMSO\text{-}d_6} = 1.0$, 0.95, 0.90, and 0.85, respectively, where $\phi_{DMSO\text{-}d_6}$ is the volume fraction of DMSO-d_6 in solvent. The errors in $I(Q)$ are ±1 standard deviation of the scattering intensities calculated during the circular averaging.

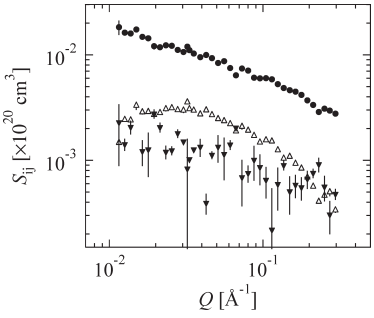

Figure 4. Partial scattering functions of CD-CD, S_{CC} (●); PEG-PEG, S_{PP} (▼); and CD-PEG, S_{CP} (△). The errors in S_{ij} are defined by the difference between the observed scattering intensities and the data reconstructed from the estimated scattering contrasts and S_{ij}.

PEG. Indeed, the ratio of $S_{CC}(Q)$ to $S_{PP}(Q)$ is nearly equal to the square of the ratio of the volume fractions. It is important that the cross-term $S_{CP}(Q)$ for PR is positive and has a magnitude between the magnitudes of the self-terms of $S_{CC}(Q)$ and $S_{PP}(Q)$. This indicates an attractive interaction between PEG and CD, which can be attributed to a mechanically interlocked connection. Furthermore, the self-term of CD, $S_{CC}(Q)$, exhibits almost the same Q-dependence as the self-term of PEG, $S_{PP}(Q)$. This exhibits that CDs in PR have the same spatial distribution as PEG segments in solution. In other words, CDs are not localized but are distributed randomly along the entire PEG chain. This result is different from the one presented in ref 20, which suggests that CDs aggregates in concentrated solutions. The polymer concentration may play an important role in the distribution of CDs in polyrotaxane. These findings obtained by SANS with contrast variation are the first direct evidence of CDs in PR dispersed randomly along the chain in solution. In order to analyze the details of $S_{CC}(Q)$ and $S_{CP}(Q)$, we performed a numerical calculation of the scattering functions of CDs that are discontinuously distributed along the polymer chains. The results of this analysis and numerical calculation will be published elsewhere.

In summary, we performed contrast variation SANS measurements on PR solutions in order to determine the detailed structure of PEG and CD in PR. $I(Q)$'s of h-PR and d-PR in mixtures of DMSO-d_6 and DMSO were successfully decomposed into partial scattering functions $S_{ij}(Q)$ of the components of PR. The CD-PEG cross-term $S_{CP}(Q)$ was positive, which corresponds to a mechanically interlocked connection between PEG and CD. In addition, the self-term of CD, $S_{CC}(Q)$, showed almost the same Q-dependence as the self-term of PEG, $S_{PP}(Q)$. This indicated

that the CDs in PR were distributed randomly along the PEG chain. Contrast variation SANS is an efficient technique for investigating static structures of components of supramolecular systems; for example, it has proved effective in studying the conformations of components of a system and the correlations among them.

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