Title	β-シクロデキストリンとポリエチレングリコール-ポリプロピレングリコール トリブロック共重合体からなるポリロタキサンの合成とその温度応答特性
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Synthesis and Thermo-Responsive Properties of Polyrotaxanes Consisting of β-Cyclodextrins and a Poly(ethylene glycol)-Poly(propylene glycol)Triblock-Copolymer

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Abstract

Stimuli-responsive polymers have been studied as smart materials aiming at the application in biomedical fields or chemomechanical devices. The representative of the stimuli-responsive polymers is poly(*N*-isopropylacrylamide) and its copolymers, in which the coil-globule transition based on hydration-dehydration behavior is induced in response to temperature. Such a stimuli-responsive mechanism involves long relaxation time for the transition of the polymeric chain into solvent. The chemomechanical devices have been designed as hydrogels crosslinked with the temperature-responsive polymers. In these hydrogels, the characteristic time of swelling-deswelling is typically governed by diffusion-limited transport of the polymeric components of the network in water. Since the polymer chain in the hydrogels is fixed at the both terminals, rate-determining step for the swelling-deswelling involves the relaxation of the polymer chains. This physicochemical property is likely to limit the advances in the design of actuators for chemomechanical devices. One of the ideal chemomechanical systems will be a natural architecture of muscle contraction where myosin headpieces slide along actin filaments to initiate the contraction process. Such a sliding function is considered to be advantageous for energy balance compared with any other stimuli-responsive mechanisms.

In order to achieve such a molecular sliding function as a stimuli-responsive device, a polyrotaxanes in which many - cyclodextrins (β-CDs) were threaded onto a triblock-copolymer of poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG) capped with fluorescein-4-isothiocyanate (FITC) was synthesized as a candidate for biomimetic engineering materials. Polyrotaxanes are defined as a molecular assembly in which many cyclic molecules are threaded onto a linear polymeric chain capped with bulky end-groups. My concern regarding polyrotaxanes is how such a molecular assembly can be utilized as a material with molecular dynamic functions: threading of many CDs onto a polyrotaxane might change the location along a linear polymeric chain in response to external stimuli which would be perceived as the action of mechanical pistons. In this study, the thermally-

induced localization of β-CDs in the polyrotaxane was analyzed by circular dichroism and 750 MHz ^{1}H-NMR spectroscopy. In addition, the temperature dependent association behavior of the polyrotaxane was discussed in relation to the location of β-CDs along the triblock-copolymer by light scattering measurements.

Synthesis and characterization of the FITC-introduced polyrotaxane: The polyrotaxane was synthesized by coupling of FITC with the terminal amino groups in the polypseudorotaxane. The threading of β-CDs onto the triblock-copolymer was confirmed by gel permeation chromatography and 2D NOESY NMR spectrum. The number of β-CDs in the polyrotaxane was determined from the ^{1}H-NMR spectrum. The polyrotaxane was soluble in polar solvents such as dimethyl sulfoxide (DMSO), dimethylformamide (DMF) and 0.01 M NaOH over a wide range of temperature, which means that the intermolecular forces such as hydrogen bonding between neighboring β-CDs were partially eliminated. As a model polymer, FITC-introduced triblock-copolymer was synthesized.

Change in the location of β-CDs in the polyrotaxane with temperature: In order to clarify a change in the location of β-CD molecules in the polyrotaxane in response to temperature, the interaction between β-CDs and the terminal FITC moiety was analyzed in the alkaline condition below critical association concentration (CAC). From the results of temperature dependence of induced circular dichroism and 750 MHz ^{1}H-NMR spectra, interaction of the β-CDs with the terminal FITC moiety in the polyrotaxane was confirmed at low temperature. However, the interaction of the β-CDs with the PPG segment in the polyrotaxane was observed with increasing temperature. From these results, it is considered that β-CD molecules were localized on the PPG segment with increasing temperature. The movement of β-CDs towards the PPG segment is supported by the enhanced polypseudorotaxane formation between β-CDs with the triblock-copolymer at elevated temperature. A temperature rise was found to contribute to an increase in the number of threaded β-CDs in the polypseudorotaxane. Based on these results, it is considered that the hydrophobic interaction between β-CDs and the PPG segment in the polyrotaxane plays a dominant role in the complexation, and is enhanced by temperature.

Association behavior of the polyrotaxane in relation to location of β-CDs: Intermolecular association of the polyrotaxane was characterized in the alkaline condition above the CAC. From the results of static- and dynamic- light scattering measurements, the association number of the polyrotaxane was found to be smaller than that of the model triblock-copolymer at any temperature. The decreased association number of the polyrotaxane is considered to be due to the effect of the polyrotaxanation. Presumably, the threaded β-CDs can prevent the hydrophobic interaction between the PPG segment with increasing temperature. Interestingly, the association number of the polyrotaxane was decreased with increasing temperature from 35 °C to 50 °C although that of the model triblock-copolymer was slightly increased. Further, it was found that the cumulant diameter and polydispersity index of the polyrotaxane was decreased with increasing temperature from 35 °C to 50 °C. It is noted that the majority of β-CDs in the polyrotaxane move toward the PPG segment around 50 °C below the CAC. The dissociation behavior of the polyrotaxane may be related to the localization of β-CDs along the triblock-copolymer.

Presumably, the assembled β-CDs onto the PPG segment may inhibit the interaction between the PPG segment.

Overall, the change in the localization of β-CDs in response to temperature is likely to control the intermolecular forces between the polyrotaxane molecules. These findings are of great important in the design of nano-organized systems based on the molecular dynamic function.

Publication list

Original articles

[1] H. Fujita, T. Ooya, M. Kurisawa, H. Mori, M. Terano and N. Yui: "Thermally switchable polyrotaxane as a model of stimuli-responsive supramolecules for nano-scale devices" *Macromol. Rapid Commun.,* **17**,509-515 (1996).

[2] H. Fujita, T. Ooya, M. Kurisawa and N. Yui, "Stimuli-responsive properties of polyrotaxanes consisting of β-Cyclodextrins and hydrophilic-hydrophobic block-copolymer" *Advances in Polymeric Biomaterials Science* T. Akaike, T. Okano, M. Akhi, M. Terano and N. Yui, Eds., CMC, Tokyo, 1997, pp. 649-656.

[3] H. Fujita, T. Ooya and N. Yui, " Synthesis and characterization of a polyrotaxanes consisting of β-cyclodextrins and a poly(ethylene glycol)-poly(propylene glycol) triblock-copolymer" *Macromol. Chem. Phys.,* in press (1998).

[4] H. Fujita, T. Ooya and N. Yui, "Thermo-induced localization of cyclodextrins in a polyrotaxane consisting of β-cyclodextrins and poly(ethylene glycol)-poly(propylene glycol) triblock-copolymer" *Macromolecules,* submitted (1998).

[5] H. Fujita, T. Ooya and N. Yui, "Association behavior of a polyrotaxane consisting of β -cyclodextrins and a poly(ethylene glycol)-poly(propylene glycol) triblock-copolymer" *Polym. J.,* submitted (1998).

Review

[1] T. Ooya, H. Fujita and N. Yui, "Design of Stimuli-Responsive Polyrotaxanes-New Trend in Supramolecular Materials" *Hyomen*(Surface in Japanese) submitted (1998).

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