

Thermally-Responsive Properties of a Polyrotaxane Consisting of β -Cyclodextrins and a Poly(ethylene glycol)-Poly(propylene glycol) Triblock-Copolymer*

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ABSTRACT: A polyrotaxane, in which many β -cyclodextrin molecules (β -CDs) are 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 model of stimuli-responsive molecular assemblies for nano-scale devices. The interaction between the β -CDs and the terminal FITC moieties was significantly observed at low temperature in the diluted condition. However, the interaction of the β -CDs with the PPG segment was observed with increasing temperature. From these results, it is considered that the majority of the β -CDs move toward the PPG segment with increasing temperature. Intermolecular association behavior of the polyrotaxane was characterized by static and dynamic light scattering measurements above critical association concentration. The polyrotaxane associated at lower temperature showed dissociation behavior above a specific temperature. Based on these results, it is suggested that the dissociation of the associated polyrotaxane molecules is closely related to the thermally-induced localization of β -CDs onto the PPG segment.

KEY WORDS Stimuli-Responsive Polymer / Polyrotaxane / β -Cyclodextrin / Triblock-Copolymer / Thermally-Responsive Localization / Association Behavior /

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 polymers¹. 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.

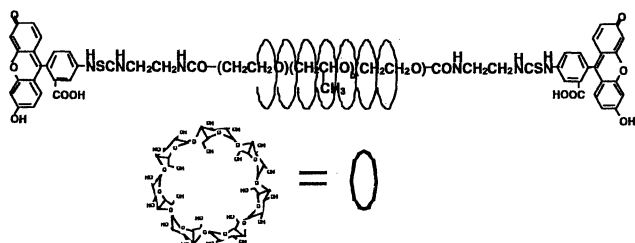
In order to achieve such a molecular sliding function as a stimuli-responsive device, we have studied stimuli-responsive polyrotaxanes consisting of β -cyclodextrins (β -CDs) and a triblock-copolymer of poly(ethyleneglycol) (PEG) and poly(propylene glycol) (PPG)^{2,3}. Polyrotaxanes are defined as a molecular assembly in which many cyclic molecules are threaded onto a linear polymeric chain capped

with bulky end-groups. Our 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. Those piston functions have been previously studied by Stoddart *et al.* using a rotaxane structure. They have developed molecular shuttles using rotaxanes in which a π -electron-rich macrocycle on a π -electron-deficient backbone moves back and forth reversibly in response to external stimuli⁴. As far as we consider chemomechanical devices based on the molecular piston functions, polyrotaxanes can be more advantageous than rotaxanes in terms of a change in solution properties. In the last decade, Gibson *et al.*, Ritter *et al.* and Harada *et al.* have contributed to the novel development of polyrotaxanes. Gibson *et al.* studied solvent-switchable polyrotaxanes utilizing polyurethanes and crown ether⁵. Ritter *et al.* studied side-chain polyrotaxanes utilizing CDs and a polymethacrylate or poly(ether sulfone) as a main chain^{6,7}. Harada *et al.* investigated macromolecular recognition by CDs with PEG⁸, PPG⁹, Pluronic® (PEG-*block*-PPG-*block*-PEG and PPG-*block*-PEG-*block*-PPG)⁸, poly(alkyl vinyl ether)¹⁰ and polyester¹¹ as a family of polyrotaxanes. Based on the Harada's studies, Topchieva and her co-workers have studied inclusion complexation between Pluronic® and CDs¹². In our previous study, the polyrotaxane in which many β -CDs are threaded onto the triblock-copolymer capped with fluorescein-4-isothiocyanate (FITC) was synthesized and characterized in terms of a change in the location of β -CD molecules in response to temperature (Scheme 1)^{13,14}. Because the driving force for polypseudorotaxane formation between β -CDs and the triblock-copolymer is due to intermolecular

* This paper is dedicated to Professor Teiji Tsuruta in honor of his 80th birthday.

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hydrogen bonding between neighboring β -CDs as well as steric fittings and a hydrophobic interaction⁸, several stimuli such as temperature may be used to control the assembled state of CD onto a polyrotaxane. Since the number of threaded β -CD molecules per the triblock-copolymer was enhanced by temperature in polypseudorotaxane formation between β -CDs and the triblock-copolymer, thermally-induced localization of β -CD onto the triblock-copolymer in the polyrotaxane is readily anticipated.



Scheme 1. Chemical structure of the polyrotaxane.

The synthesized polyrotaxane was soluble in polar solvents such as dimethyl sulfoxide (DMSO), dimethylformamide (DMF) and NaOH aq. (pH 12-13) over a wide range of temperature. This means that intermolecular forces between neighboring β -CDs were partially eliminated. In the alkaline condition, the interaction between β -CDs with the terminal FITC moiety was observed at low temperature. However, with increasing temperature, a significant interaction of the β -CDs with the PPG segment in the polyrotaxane was observed. From 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 assemble state of β -CDs onto the PPG segment^{13,14}. This physicochemical property indicates that the assembled and dispersed states of the β -CDs along the triblock-copolymer are thermally-switchable in the polyrotaxane. Presumably, hydrated water molecules with the PPG segment at lower temperature may be dehydrated due to the movement of β -CDs toward the PPG segment in the polyrotaxane with increasing temperature (Figure 1a). The hydration-dehydration behavior seems to be quite different from that of the above-mentioned temperature-responsive polymers (Figure 1b).

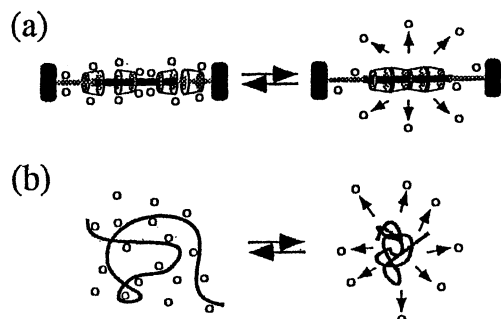


Figure 1. Hydration-dehydration behavior of (a) the polyrotaxane and (b) the conventional temperature-responsive polymer.

The polymeric component of the triblock-copolymer

named Pluronic[®] shows association behavior in water with increasing temperature due to hydrophobic interaction between the PPG segments, and leads to the formation of spherical micelles consisting of hydrophobic PPG core and hydrophilic PEG shell¹⁵. Taking the enhanced interaction of the β -CDs with the PPG segment in the polyrotaxane into account, it is expected that the thermally-induced localization of β -CDs may affect the association behavior of the polyrotaxane molecules. In this paper, intermolecular association of the polyrotaxane was characterized in an alkaline condition. Critical association concentration (CAC) was determined by static light scattering measurements. Below CAC, interaction between the β -CDs with the PPG segment in the polyrotaxane was characterized by 750MHz ¹H-NMR spectroscopy. Above CAC, static and dynamic light scattering measurements were carried out. From the obtained data, the temperature-dependent association behavior of the polyrotaxane was discussed in relation to the location of β -CDs along the triblock-copolymer.

EXPERIMENTAL

Synthesis of the polyrotaxane

The polyrotaxane was synthesized according to our previously method^{13,14}; terminal hydroxyl groups of the PEG-*block*-PPG-*block*-PEG triblock-copolymer (Mn = 4200, PPG segment Mn = 2250, PEG segment Mn = 975 x 2) named Pluronic[®] P-84 were activated by *N,N'*-carbonyldiimidazole in THF. The activated triblock-copolymer was allowed to react with ethylenediamine to obtain amino-terminated triblock-copolymer. The polypseudorotaxane between the amino-terminated triblock-copolymer and β -CDs was prepared in 0.1 M phosphate buffered saline (PBS) at 40 °C. The terminal amino-groups in the polypseudorotaxane were allowed to react with FITC in DMF at 5 °C. The threading of β -CDs in the polyrotaxane was confirmed by GPC [Column: GF-710HQ (Showa Denko Co., Ltd., Tokyo, Japan), Eluent: DMF] and ¹H-NMR (Solvent: DMSO-*d*₆), 2D NOESY NMR spectroscopies (Solvent: D₂O + NaOD) using a 750 MHz FT-NMR spectrometer (Varian, unity plus, CA, USA). From the 2D NOESY NMR spectrum, it was found that inner-cavity H-3 and H-5 protons of β -CD were correlated with the resonance of methyl protons of the PPG segment¹³. The number of β -CDs in the polyrotaxane was determined to be ca. 7 from the ¹H-NMR spectrum. As a model polymer, FITC-introduced triblock-copolymer was synthesized according to our previously method^{13,14}.

Determination of critical association concentration of the polyrotaxane

Concentration dependence of scattered light intensity of the polyrotaxane and the model triblock-copolymer was measured using a light scattering instrument (DLS-7000, Otsuka Electronics, Co. Osaka, Japan) equipped with 10 mW He-Ne laser at 633 nm at 25 °C in NaOH aqueous solution (pH 12-13).

Temperature-dependent localization of β -CDs in the polyrotaxane by 750 MHz $^1\text{H-NMR}$ spectra

$^1\text{H-NMR}$ spectra (750 MHz) of the polyrotaxane (0.01 wt. % in $\text{D}_2\text{O}+\text{NaOD}$) were measured at various temperature. The localization of β -CDs onto the PPG segment was determined by comparing the peak area of the shifted methyl proton peak with the unshifted methyl proton peak.

Effect of temperature on the polypseudorotaxane formation

The polypseudorotaxane between β -CDs and the triblock-copolymer was prepared at various temperature for 48 h in NaOH aq. (pH 12-13) (molar ratio of the triblock-copolymer / β -CDs in feed was 1 / 20). The number of β -CDs in the precipitated polypseudorotaxane was calculated from the $^1\text{H-NMR}$ spectra.

Intermolecular association of the polyrotaxane

The weight-average molecular weight (M_w), association number, second virial coefficient (A_2) and the radius of gyration (R_g) of the polyrotaxane and the model triblock-copolymer were determined at various temperature by static light scattering measurements equipped with 10 mW He-Ne laser at 633 nm. The dn/dc values at various temperatures were determined to be 0.150 ml/mg. The association number was calculated from the obtained M_w and the number-averaged molecular weight. Dynamic light scattering measurements were carried out to determine cumulant diameter, polydispersity index and diffusion coefficient at various temperature.

RESULTS AND DISCUSSION

Critical association concentration of the polyrotaxane

Critical association concentration (CAC) of the polyrotaxane and the model triblock-copolymer was determined from concentration dependence of the scattered light intensity in the alkaline condition (pH 12-13) at 25°C . According to the reports by Zhou *et al.*, an increase in the scattered light intensity indicates the association of a triblock-copolymer^{16,17}. The scattered light intensity of the polyrotaxane and the model triblock-copolymer was drastically increased in the concentration above 0.5 and 0.01 mg/ml, respectively. From these results, the CAC of the polyrotaxane and the model triblock-copolymer were determined to be ca. 0.5 and 0.01 mg/ml, respectively.

Characterization of thermally-induced localization of β -CDs in the diluted condition by 750 MHz $^1\text{H-NMR}$ spectroscopy

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 in the alkaline condition was analyzed by means of 750 MHz $^1\text{H-NMR}$ spectra below CAC. The pK_a values of hydroxyl groups of β -CD and carboxyl group of FITC are ca. 12.2 and ca. 4-5 at 25°C , respectively, i.e., about 50 % of hydroxyl groups of β -CD might be ionized in this condition.

In the previous paper, the vis-absorption and induced circular dichroism (ICD) spectra of the polyrotaxane in the

alkaline condition were confirmed around 490 nm^{13,14}. The ICD spectra of the polyrotaxane showed a positive ellipticity $[\theta]$ around at 490 nm which corresponds to the vis-absorption. Because the ICD spectrum was not observed in the model triblock-copolymer in the presence of β -CD, it is suggested that the positive ellipticity $[\theta]$ of the polyrotaxane is due to interaction of the terminal FITC moiety with β -CDs at low temperature. Further, it was found that the positive ellipticity $[\theta]$ of the polyrotaxane was decreased when the temperature increased from 10 to 50°C . From this, the interaction between β -CDs and the terminal FITC moiety in the polyrotaxane is considered to decrease with increasing temperature.

Figure 2 shows the $^1\text{H-NMR}$ spectra of the methyl protons in the polyrotaxane at 10, 30 and 50°C . With increasing temperature, the peak of the methyl protons in the PPG segment shifted to the lower field and slightly broadened for the polyrotaxane. As for the model triblock-copolymer, no change for the peak of the methyl protons was observed with increasing temperature. Harada *et al.* reported that the methyl- and methylene- protons of side alkyl groups in a polymer chain were shifted to a lower field by the addition of α -CDs in D_2O ¹⁸. This report indicates that α -CDs include the side alkyl groups in the polymer chain. Taking this report into account, the methyl proton peak shifted to the lower field for the polyrotaxane is considered to be due to the interaction between the methyl protons of propylene glycol (PG) units and the cavity of the β -CDs. Assuming that the shifted methyl proton peak is the included methyl protons with β -CDs, the number of β -CDs located on the PG units can be estimated by calculating the relative area of the shifted methyl proton peak (A_1).

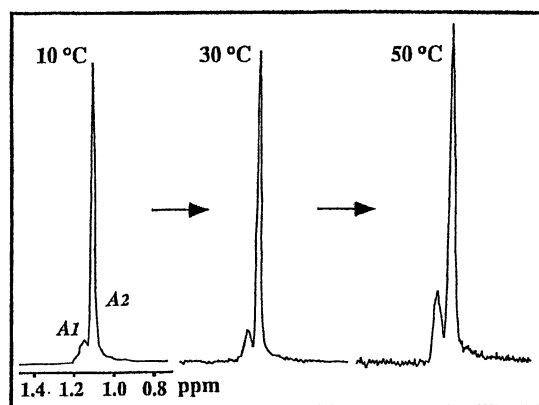


Figure 2. Temperature dependent of the $^1\text{H-NMR}$ peak shapes of the methyl protons in the polyrotaxane.

The relative A_1 peak area was calculated by the following equation (1):

$$\text{Relative } A_1 \text{ peak area (\%)} = 100 \times A_1 / (A_1 + A_2) \quad (1)$$

where A_2 is the area of the original methyl proton peak. If all the threading β -CDs (ca. 7) are localized on the PPG segment, the relative A_1 peak can be maximally 36 % assuming one β -CD molecule is threaded onto the two PG

units (total units of PG: ca. 39). The value of the relative A_1 peak area increased from 7 % to 27 % with increasing temperature from 10 to 50 °C. At 50 °C, the relative A_1 peak area (27 %) corresponds to 74 % of the maximum peak area (36 %). From this, it is considered that ca. 5.2 β -CD molecules were localized on the PPG segment at 50 °C. Presumably, the number of β -CD molecules on the PPG segment will be determined by the balance of the following two forces: the enhanced hydrophobic interaction between the β -CD cavity and the PPG segment, and the repulsive forces between the ionized hydroxyl groups in β -CD in the alkaline condition.

The movement of β -CDs toward the PPG segment with increasing temperature is supported by the enhanced polypseudorotaxane formation between β -CDs with the triblock-copolymer at elevated temperature. Figure 3 summarizes the temperature dependence of the polypseudorotaxane formation between β -CDs and the triblock-copolymer in the alkaline condition. A temperature rise was found to contribute to an increase in the number of threaded β -CDs in the polypseudorotaxane (molar ratio of the triblock-copolymer / β -CDs in feed is 1 / 20). From this figure, 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. Therefore, it is imagined that the majority of β -CDs move toward the PPG segment with increasing temperature although some β -CDs may reside on the PEG segments, as shown in Figure 4.

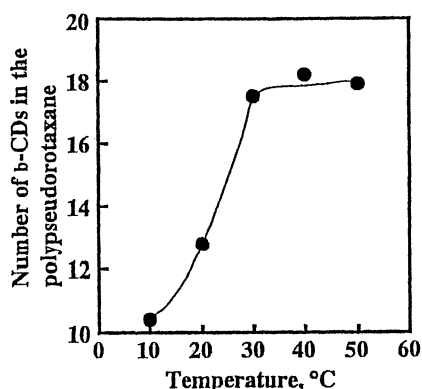


Figure 3. The effect of temperature on the formation of the polypseudorotaxane in NaOH aq. (pH 12-13) for 48 h.

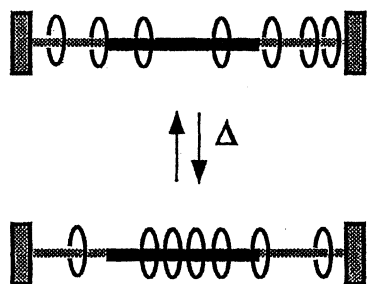


Figure 4. Thermally-responsive characteristic of the polyrotaxane.

Association behavior of the polyrotaxane above CAC

Intermolecular association of the polyrotaxane in the alkaline condition was characterized above the CAC (ca. 0.5 – 4.0 mg/ml). Solution parameters such as M_w , A_2 and R_g values of the polyrotaxane were summarized in Table I.

Table I. Solution parameter of the polyrotaxane

Temp. (°C)	$M_w \cdot 10^3$ ^a (g·mol ⁻¹)	Calculated $M_n \cdot 10^{-4}$	Association number ^b	R_g (nm)
10	2.0	1.31	15	46.9
25	10.7	1.31	82	47.5
35	27.5	1.31	209	53.8
50	8.5	1.31	65	40.7

^aThose values were determined from Zimm plots.

^bThe association number was calculated from M_w and number-average molecular weight of the polyrotaxane.

Figure 5 summarizes a change in the association number of the polyrotaxane and the model triblock-copolymer as a function of temperature. The association number of the polyrotaxane was found to be much smaller than that of the model triblock-copolymer. Ritter *et al.* studied the effect of the threading of 2,6-dimethyl- β -cyclodextrin (Me_2 - β -CD) on intermolecular association of a methacrylic polymer derivative¹⁹. A semi-rotaxane consisting of Me_2 - β -CD and triphenylmethylmethyl-aminoundecanamide as a side chain was introduced into the methacrylic polymer. They found that the side chain polyrotaxane has a lower reduced viscosity in comparison with the parent polymer. This phenomenon indicates that hydrogen bonding between amide groups in the side-chain are prevented by the threading of Me_2 - β -CD onto the side chain. Taking this report into account, the reduced association number of the polyrotaxane is considered to be due to the prevention of intermolecular forces between the polyrotaxane molecules by the threading of β -CDs.

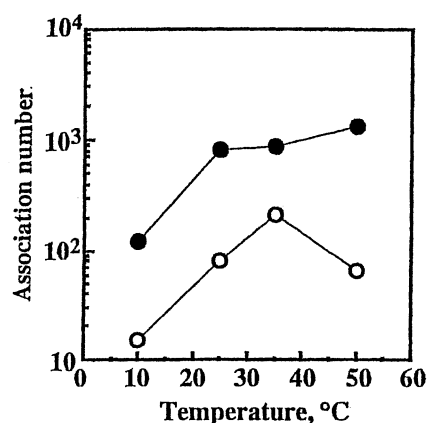


Figure 5. Change in the association number of the polyrotaxane (○) and the model triblock-copolymer (●).

In the temperature range from 35 °C to 50 °C, the association number of the polyrotaxane was decreased although that of the model triblock-copolymer was slightly

increased. It is obvious that the intermolecular association behavior of the polyrotaxane is quite different from that of the model triblock-copolymer. Generally, Pluronic® shows an increase in the association number and the cumulant diameter with increasing temperature due to the enhanced hydrophobic interaction between the PPG segment^{16,17}. The temperature dependence in the association number, cumulant diameter and polydispersity index of Pluronic® (P-84) was confirmed in the same condition. From this, it is considered that the increase in the association number of the model triblock-copolymer with increasing temperature corresponds to the temperature-dependent association of the triblock-copolymer. As for the polyrotaxane, it is considered that the intermolecular forces between the polyrotaxane molecules were reduced with increasing temperature from 35 to 50 °C.

This reduced-association number of the polyrotaxane was also confirmed by the results of dynamic light scattering measurements. Figure 6 summarizes the cumulant diameter and polydispersity index of the polyrotaxane as a function of temperature. The decreased cumulant diameter and the increased polydispersity index were observed above 40 °C. These results suggest the dissociation of the polyrotaxane molecules above this temperature.

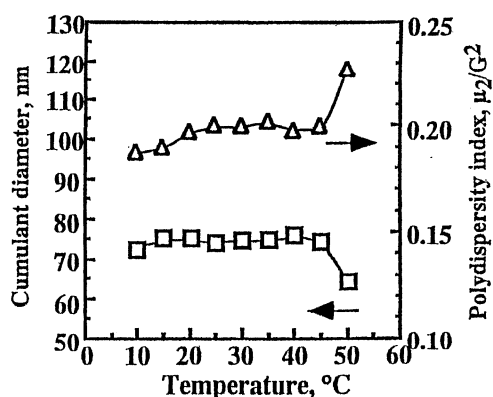


Figure 6. Change in the cumulant diameter (\square) and the polydispersity index of the polyrotaxane (\triangle). (Detection angle 90°, concentration 1.0 mg/ml).

This suggestion is further supported by a change in the diffusion coefficient (D_T) of the polyrotaxane with increasing temperature from 10 to 50 °C (Figure 7). The thermal stability of the associated polyrotaxane was confirmed by the concentration dependence of the D_T value. The D_T value of the polyrotaxane was drastically increased when the concentration was diluted from 4.0 to 0.5 mg/ml as temperature increased from 10 to 50 °C. Kopecek *et al.* have reported that the copolymer of *N*-(2-hydroxypropyl)-methacrylamide (HPMA) containing oligopeptide sequences as side chains forms micelles with increasing the number of the side chain²⁰. Moreover, they reported that the D_T value of the micelle was drastically increased in diluted region by the decomposition of the micelle, i.e., the micelle is dissociated in the diluted region. Taking this phenomenon

into account, the increase in the D_T value in diluted region at higher temperature indicates the dissociation of the associated polyrotaxane molecules. The diffusion at infinite dilution D_0 was determined to be $12.2 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ at 50 °C. The hydrodynamic radius (R_h) was calculated to be 35.7 nm using Stokes-Einstein equation. The ratio of R_g and R_h (R_g/R_h) reflects the molecular shape^{21,22}. As for the polyrotaxane, the R_g/R_h at 50 °C was calculated to be 1.14. This value may indicate that the polyrotaxane associated at 50 °C does not have a spherical shape since the R_g/R_h value of a hard sphere such as micelles is ca. 0.776, i.e., the association of the polyrotaxane at 50 °C is not the core-shell type micelle.

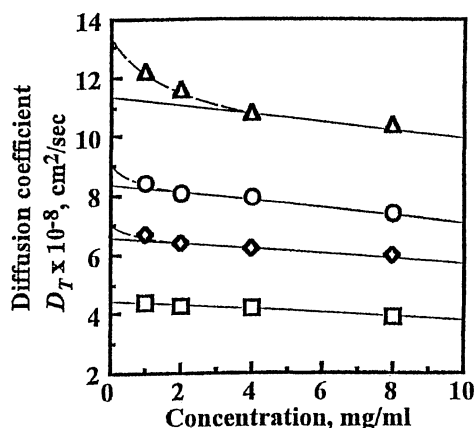


Figure 7. Plots of translational diffusion coefficient (D_T) against the concentration of the polyrotaxane at 10°C (\square), 25°C (\diamond), 35°C (\circ), 50°C (\triangle). (Detection angle 90°).

It is mentioned above that the majority of β -CDs in the polyrotaxane move toward the PPG segment around 50 °C below 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. Since the number of β -CD molecules in the polyrotaxane was unexpectedly low (ca. 7) and 5 β -CD molecules were located onto the PPG segment around 50 °C, the effect of β -CD threading on the dissociation behavior would appear at relatively higher temperature range (40 - 50 °C).

Overall, it is concluded that the dissociation of the associated polyrotaxane molecules is closely related to the movement of β -CDs toward the PPG segment (Figure 8). The change in the localization of β -CDs in response to temperature is likely to control the intermolecular forces between the polyrotaxane molecules.

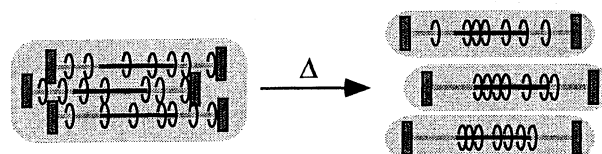


Figure 8. The dissociation behavior of the polyrotaxane.

CONCLUSIONS

A polyrotaxane consisting of β -CDs and a triblock-copolymer of PEG and PPG capped with FITC was synthesized, and intermolecular association behavior of the polyrotaxane was analyzed in alkaline condition in relation to the localization of β -CDs. Critical association concentration of the polyrotaxane was determined to be 0.5 mg/ml, which was a much higher value than that of the model triblock-copolymer. It was found that the majority of the β -CDs moved toward the PPG segment with increasing temperature below CAC. Above CAC, the polyrotaxane showed dissociation behavior with increasing temperature from 35 to 50 °C. It is considered that the movement of β -CDs toward the PPG segment affects the thermally-induced association of the PPG segment above CAC. Therefore, the dissociation behavior of the polyrotaxane is suggested to be closely related to the thermally-induced location of β -CDs onto the PPG segment. These findings are of great importance in the design of nano-organized systems based on the molecular dynamic function.

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