Block-Selective Polypseudorotaxane Formation in PEI-*b*-PEG-*b*-PEI Copolymers via pH Variation

Sang Cheon Lee, Hak Soo Choi, Tooru Ooya, and Nobuhiko Yui*

School of Materials Science and the 21st Century COE Program, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Tatsunokuchi, Ishikawa 923-1292, Japan

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ABSTRACT: An ABA triblock copolymer, consisting of linear polyethylenimine (PEI) and poly(ethylene glycol) (PEG) (PEI-*b*-PEG-*b*-PEI), was examined for pH-dependent polypseudorotaxane formation with α-cyclodextrins (α-CDs). Although no complexation was observed for the mixture of α-CDs and PEI homopolymers, the polypseudorotaxane of PEI-*b*-PEG-*b*-PEI copolymer was prepared at pH below 8.0. ^{1}H NMR analysis showed that the stoichiometry for the polypseudorotaxane was about 2:1 ([EG + EI]:[α-CD]) at pH 11.0. Interestingly, the stoichiometry of [EG + EI] to [α-CD] below pH 8.0 was found to be about 4:1, which matched well with the assumption that the complex formation is ascribed only to the PEG block. X-ray diffraction and ^{13}C CP/MAS measurements verified that the control of pH affected the polypseudorotaxane formation, and the ionization state of the PEI block was the key factor to determine the threading and dethreading process of α-CDs onto polymer chains. Each block in the copolymer acted as a guest for α-CDs at pH 11.0, whereas α-CDs on the PEI block were dethreaded exclusively to result in block-selective polypseudorotaxane formation based on the PEG middle block at pH below 8.0, where the secondary amines in the PEI block was protonated (pK_a 8.9). The threading/dethreading process of CDs along the PEI chains could be reversibly controlled by adjusting pH. Such unique pH-controllable polypseudorotaxane formation may be useful in designing many building blocks for stimuli-responsive polyrotaxanes.

Introduction

The inclusion complexation of cyclodextrins (CDs) with linear polymers is a topic of rapidly growing interest in the field of supramolecular self-assembly, especially for constructing polypseudorotaxanes and polyrotaxanes.[1] To date, a diverse class of linear polymers of hydrophilic or hydrophobic nature has been found to form polypseudorotaxanes with their corresponding CDs with specific selectivity.[2,3] The inclusion complexation has been known to arise from the cooperation of a variety of driving forces such as the steric fitting as well as the hydrophobic interaction between the cavity of CDs, and polymer chains.[4] Thus, the many stimuli, such as pH and temperature, that can modulate the interaction between the interior of CDs and polymers may play a key role in controlling the assembled and dispersed states of CDs along the polymer chains. Recently, we demonstrated that α-CD could be efficiently threaded onto poly(ϵ-lysine) or linear polyethylenimine (PEI) chains in the un-ionized state to form crystalline polypseudorotaxanes, whereas α-CD could not act as a host for any protonated polymer chains (pH < 8.0).[5] This indicates that the pH decrease induces the repulsion between the ionized polymer chains and α-CDs since the cationic nature of the polymer backbones disfavors a hydrophobic α-CD cavity.[6] We believe that understanding this type of stimuli-sensitive inclusion complexation would be a good guide to the design of useful building blocks for novel functional supramolecular structures.

In recent reports, a great deal of effort has been focused on the polypseudorotaxane formation between CDs and polymers with structural heterogeneity, such as random and block copolymers.[7−9] So far, a majority of reports has been concerned simply with the threading process of CDs along the polymer chains and the subsequent formation of the polypseudorotaxanes. Since the properties of copolymer chains can be readily modulated depending on the nature of each polymer component, its relevant combination may result in the polypseudorotaxanes with numerous interesting properties, which have not been possible with the current homopolymer-based polypseudorotaxanes. Recently, we reported on a thermoresponsive polyrotaxane consisting of β-CDs and a triblock copolymer of poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG).[10] It was confirmed that the location of β-CDs along the polymer chains could be readily controlled by adjusting the temperature. The majority of β-CDs moved toward the PPG middle block with increasing temperature, primarily due to the enhanced hydrophobic interaction between the β-CD cavity and the PPG segment.

In this study, we report on the pH-dependent polypseudorotaxane formation of α-CD with a linear ABA triblock copolymer consisting of PEI and PEG (PEI-*b*-PEG-*b*-PEI). We are interested in knowing whether the threading/dethreading of α-CDs in the triblock copolymer of PEG and ionizable PEI is pH-controllable to induce block-selective inclusion complexation. The significant pH dependence of polypseudorotaxane formation between α-CDs and PEI-*b*-PEG-*b*-PEI, which has never been observed for usual polypseudorotaxanes, is demonstrated.

Experimental Section

Materials and Equipment. PEG of the number-average molecular weight (M_n) of 2000 (PEG$_{2000}$) was purchased from Aldrich Co. and used after drying in vacuo at 100 °C for 24 h. Mesyl chloride (MsCl) and 2-methyl-2-oxazoline (OZ, distilled over calcium hydride) were purchased from Aldrich Co. Tri-

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* To whom correspondence should be addressed: Telephone and Fax: +81-761-51-1640. E-mail: yui@jaist.ac.jp.

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ethylamine (TEA), acetonitrile, and methylene chloride were dried and distilled over calcium hydride. A methanol solution of ammonia (2.0 M) and α-CD were purchased from Aldrich Co. and Wako Pure Chemical Co. (Tokyo, Japan), respectively, and used as received. Diethyl ether was of reagent grade.

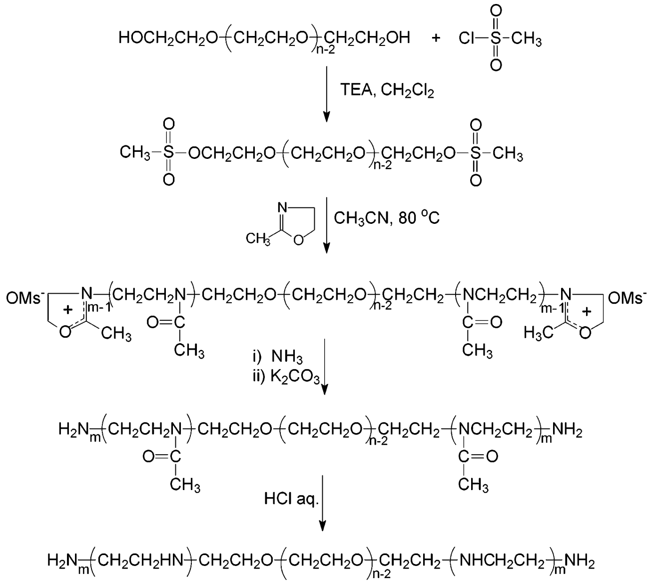
^{1}H and ^{13}C NMR spectra were obtained on a FT-NMR spectrometer (Varian, Unity plus) at 750 MHz. Molecular weights and molecular weight distributions were determined using a GPC system equipped with a refractive index detector (JASCO RI-930), a quaternary pump (JASCO PU-980), and two Ultrahydrogel linear mixed columns (Waters) in series. The pure water containing 0.1% formic acid was used as an eluent at a flow rate of 0.8 mL/min. The molecular weights were calibrated with PEG standards. X-ray diffraction measurements were performed with a powder diffractometer (RINT2000, Rigaku, Japan) and also image- plate photography using graphite-monochromatized Cu Kα radiation ($\lambda = 1.542$ Å). The solid-state ^{13}C CP/MAS NMR spectra were recorded at 100.4 MHz on a JNM-GSX 400 NMR spectrometer with a sample spinning rate of 6 kHz at 19 °C. CP spectra were acquired with a 5 ms contact time, a 10 s repetition time, and 18000 accumulations.

Synthesis of PEG_{2000}—Bis(mesylate). To a stirred solution of PEG_{2000} (40 g, 0.02 mol) and TEA (22.3 g, 0.22 mol) in dry methylene chloride (250 mL), a solution of MsCl (22.91 g, 0.2 mol) in dry methylene chloride (50 mL) was added dropwise at 0 °C. After being stirred at room temperature under nitrogen atmosphere for 24 h, the solution was filtered and precipitated in cold diethyl ether. The crude product was dissolved in methylene chloride (400 mL), followed by washing with distilled water (100 mL), 2.0 N HCl solutions (200 mL), saturated $NaHCO_3$ solutions (200 mL), and distilled water (100 mL), respectively. After being dried over anhydrous magnesium sulfate, finally, the product was isolated by precipitation into cold diethyl ether (yield 90%). ^{1}H NMR (DMSO-d_6): δ 3.16 (s, $-CH_3$ of Ms, 6H), 3.50 (m, $-CH_2CH_2O-$, of PEG, 172H), 3.66 (m, $-CH_2CH_2OMs$, 4H), 4.29 (m, $-CH_2CH_2OMs$, 4H); ^{13}C NMR (DMSO-d_6): δ 37.3, 68.8, 70.2, 70.3.

Synthesis of POZ-*b*-PEG-*b*-POZ Copolymers. As a representative example, a block copolymer denoted as $OZ_{22}-EG_{45}-OZ_{22}$, where 22 and 45 are the average numbers of repeating units in each block, was prepared by the following procedure: A solution of PEG_{2000}−bis(mesylate) (12 g, 0.005 mol) and OZ (20.4 g, 0.24 mol) in dry acetonitrile (120 mL) was placed into a flame-dried round-bottom flask. The reaction mixture was stirred at 80 °C under nitrogen for 24 h. After the reaction was cooled to 0 °C, a methanol solution of ammonia (0.03 mol) was added to the reaction mixture under nitrogen, and the solution was then stirred at room temperature for 3 h. The reaction solution was precipitated into cold diethyl ether. The crude polymer was dissolved in methylene chloride (400 mL), washed twice with a saturated aqueous $NaHCO_3$ (100 mL), and then washed with distilled water (100 mL). After the organic layer was dried over anhydrous magnesium sulfate, the triblock copolymer, $OZ_{22}-EG_{45}-OZ_{22}$, was then isolated by precipitation into cold diethyl ether (yield 98%). ^{1}H NMR (D_2O): δ 1.93 (m, $-COCH_3$), 3.38 (s br, $-CH_2CH_2$- of OZ), 3.55 (s, $-CH_2CH_2O-$). The other block copolymer denoted as $OZ_{29}EG_{45}OZ_{29}$ was synthesized in an identical manner except that a different feed molar ratio of OZ to the EO unit of PEG_{2000}−bis(mesylate) was employed (yield 97%).

Hydrolysis of POZ-*b*-PEG-*b*-POZ Copolymers. The tertiary amide groups in POZ blocks were hydrolyzed to secondary amines by heating POZ-*b*-PEG-*b*-POZ copolymers in an aqueous solution of 10% hydrochloric acid. As an example, $OZ_{29}EG_{45}OZ_{29}$ (4.0 g, 0.6 mmol) was dissolved in a mixture of concentrated hydrochloric acid (35%, 30 mL) and distilled water (70 mL). The reaction mixture was stirred at 100 °C for 24 h. The pH of the solution was increased to 10 by adding sodium hydroxide to the solution at 0 °C. The precipitated product was collected by centrifugation, washed with distilled water, and then dried in vacuo at 60 °C to give the PEI-*b*-PEG-*b*-PEI copolymer (yield 90%). ^{1}H NMR (D_2O + 0.2 M DCl): δ 2.93 (s, $-CH_2CH_2NH-$), 3.55 (s, $-CH_2CH_2O-$).

Scheme 1. Synthetic Route for the Triblock Copolymer, PEI-*b*-PEG-*b*-PEI



Preparation of Polypseudorotaxanes. pH dependence of polypseudorotaxane formation was examined by the following method: The six batches of polypseudorotaxane suspensions were first formed at pH 11.0. The pH of each suspension was then adjusted directly to desired pH, and the polypseudorotaxanes at various pH ranges were recovered after 10 min equilibration. The precipitates were collected by centrifugation, washed with a limited amount of distilled water, and then dried in vacuo at 60 °C to yield the polypseudorotaxanes of PEI-*b*-PEG-*b*-PEI copolymers.

Results and Discussion

Synthesis and Characterization of the Block Copolymer. A new type of ABA triblock copolymers of PEI and PEG was prepared by a synthetic procedure as illustrated in Scheme 1.

The first step involved the preparation of PEG−bis(mesylate) by reacting PEG_{2000} with mesyl chloride in the presence of TEA as a catalyst. ^{13}C NMR spectroscopy confirmed the complete substitution of the hydroxyl end group of PEG_{2000} with the mesyl group, which was supported by the disappearance of the signals of two methylene carbons adjacent to hydroxyl end groups ($-PEG-CH_2CH_2-OH$) appearing at 60.3 and 72.4 ppm (data not shown). New resonance signals ascribed to $-SO_2CH_3$, $-CH_2CH_2SOCH_3$, and $-CH_2CH_2SOCH_3$ appeared at 37.3, 68.8, and 70.3 ppm, respectively. From the ^{1}H NMR and GPC analyses, the molecular weight and polydispersity of the PEG_{2000}−bis(mesylate) were calculated to be 2200 and 1.05, respectively. In the second step, PEG_{2000}−bis(mesylate) was used as a macroinitiator to initiate the cationic ring-opening polymerization of 2-methyl-2-oxazoline to produce the ABA triblock copolymers, POZ-*b*-PEG-*b*-POZ. The oxazolinium living end groups in triblock copolymers were terminated by ammonia to introduce primary amine groups at both chain ends. The molecular weight and block composition of the POZ-*b*-PEG-*b*-POZ were determined by the analysis of ^{1}H NMR spectra. Figure 1a shows the typical characteristic resonance peaks of POZ-*b*-PEG-*b*-POZ. The complete disappearance of resonance signals of $-SO_2CH_3$ at 3.17 ppm indicates that all the PEG_{2000}−bis(mesylate) are involved in the initiation of oxazoline polymerization. The molar composition ratio

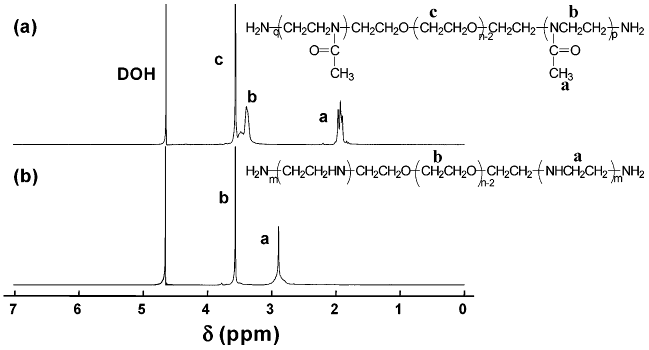


Figure 1. ^{1}H NMR spectra of $OZ_{22}EG_{45}OZ_{22}$ (a) and $EI_{22}EG_{45}EI_{22}$ (b) in D_2O containing 0.2 M DCl.

Table 1. Characteristics of POZ-*b*-PEG-*b*-POZ Triblock Copolymers

copolymer	molar ratio ([OZ]:[EG]) feed	molar ratio ([OZ]:[EG]) composition[a]	EG content (mol %)[b]	M_n[c]	M_w/M_n[d]
$OZ_{22}EG_{45}OZ_{22}$	44:45	44:45	51.6	5770	1.22
$OZ_{29}EG_{45}OZ_{29}$	60:45	58:45	56.3	6900	1.27

[a] Calculated from ^{1}H NMR spectra in D_2O. [b] The number of complexed CD in the polypseudorotaxane. [c] Molar content of EG in the block copolymer by ^{1}H NMR. [d] Estimated by GPC using PEG standards (eluent: 0.1% formic acid).

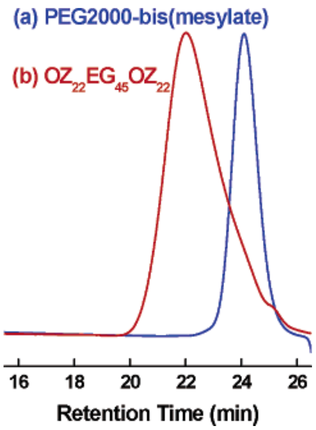


Figure 2. GPC traces of PEG_{2000}−bis(mesylate) (a) and $OZ_{22}EG_{45}OZ_{22}$ (b).

of repeating units in PEG and POZ was determined by the peak integration ratio of CH_2 in PEG at 3.49 ppm to CH_3 in POZ at 1.98 ppm. According to the ^{1}H NMR spectra, the calculated block composition ratio of POZ to PEG blocks was in a good accordance with the feed ratio (Table 1).

Figure 2 shows GPC chromatograms of a macroinitiator (PEG_{2000}−bis(mesylate)) and the resulted triblock copolymer ($OZ_{22}EG_{45}OZ_{22}$). The block copolymers exhibit typical chromatograms with relatively narrow polydispersity (Table 1), and there is negligible trace for the residual PEG_{2000}−bis(mesylate) macroinitiator. This confirms the high efficiency of PEG−bis(mesylate) in initiating the cationic living polymerization of OZ.

The triblock copolymer, PEI-*b*-PEG-*b*-PEI, was prepared by the alkaline hydrolysis of POZ-*b*-PEG-*b*-POZ. Figure 1b shows the ^{1}H NMR spectra of $EI_{22}EG_{45}EI_{22}$ after alkaline hydrolysis of $OZ_{22}EG_{45}OZ_{22}$. The resonance signals at 1.98 ppm (Figure 1a) ascribed to methyl groups in POZ blocks completely disappeared after hydrolysis, and the signals of methylene protons adjacent to the nitrogen in POZ shifted from 3.32 to 2.66 ppm. These results prove the 100% transformation of tertiary amide groups in POZ to secondary amine groups in PEI. The N/C ratios for $EI_{22}EG_{45}EI_{22}$ and $EI_{29}EG_{45}EI_{29}$, calculated on the basis of copolymer compositions, were found to be 19.8% and 22.0%, respectively, in reasonable agreement with the ^{1}H NMR results.

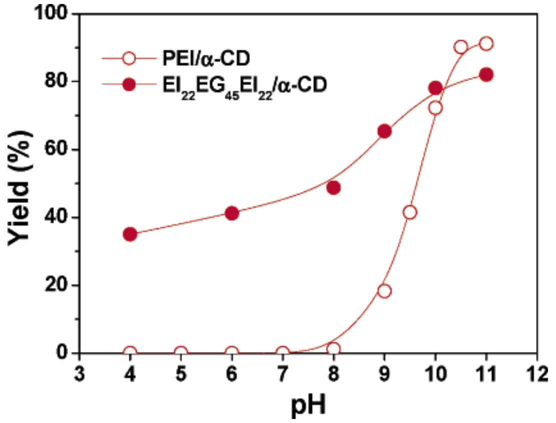


Figure 3. pH-dependent changes in the yield of the polypseudorotaxanes of PEI homopolymer (M_n 3200)/α-CD (○) and $EI_{22}EG_{45}EI_{22}$/α-CD (●).

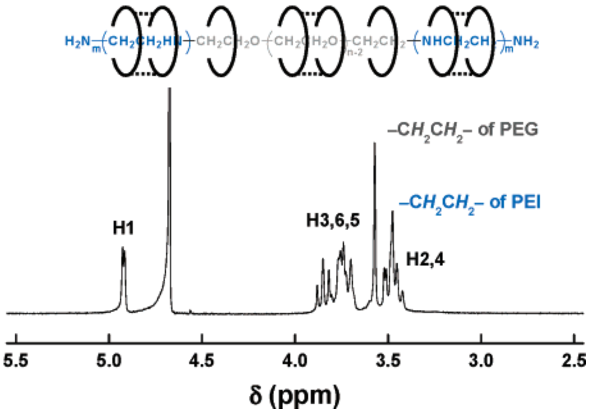


Figure 4. ^{1}H NMR spectrum of the polypseudorotaxane of $EI_{22}EG_{45}EI_{22}$ with α-CD in D_2O containing 0.2 M DCl.

pH-Dependent Polypseudorotaxane Formation. Figure 3 shows pH-dependent changes in the yield of the polypseudorotaxanes of α-CD with $EI_{22}EG_{45}EI_{22}$ or a linear PEI homopolymer (M_n 3200). Striking changes in the yields of the polypseudorotaxanes were observed around pH 9.0. The yield exhibited a maximum at pH 11.0. It is of great interest to note that α-CDs formed polypseudorotaxane precipitates with $EI_{22}EG_{45}EI_{22}$ even at a pH below 8.0, whereas no complex formation was observed for the mixture of α-CDs and a PEI homopolymer due to the energetically disfavorable interaction between the cavities of α-CDs and the ionized PEI chains.[5b] Thus, it is likely that the polypseudorotaxane formation below pH 8.0 occurred exclusively through inclusion complexation between α-CDs and the middle PEG block in the block copolymer.

Stoichiometry. The structural compositions of the polypseudorotaxanes were calculated from ^{1}H NMR spectra (Figure 4). The peak integral ratio of the methylene protons in PEG (3.55 ppm) to C−1(H) of α-CD (4.82 ppm) was used to calculate the stoichiometry. ^{1}H NMR analysis showed that the stoichiometry for complex formation between $EI_{22}EG_{45}EI_{22}$ and α-CD was about 2:1 ([EG + EI]:[α-CD]) at pH 11.0, as shown in Table 2. Strikingly, on an assumption that the inclusion

Table 2. pH Dependence of Stoichiometry in $EI_{22}EG_{45}EI_{22}$/α-CD Polypseudorotaxanes

[EG + EI]:[α-CD][a]					[EG]:[α-CD][a]		
pH 11	pH 9	pH 8	pH 6	pH 4	pH 8	pH 6	pH 4
2.1	3.1	4.2	4.1	4.1	2.1	2.0	2.0

[a] The threading ratios of α-CD to [EG + EI] or [EG] were determined by the peak integration ratios of C(1)−H of α-CD at 4.88 ppm to $-CH_2CH_2-$ of the polymer at 3.54 ppm in ^{1}H NMR spectra (D_2O containing 0.2 M DCl).

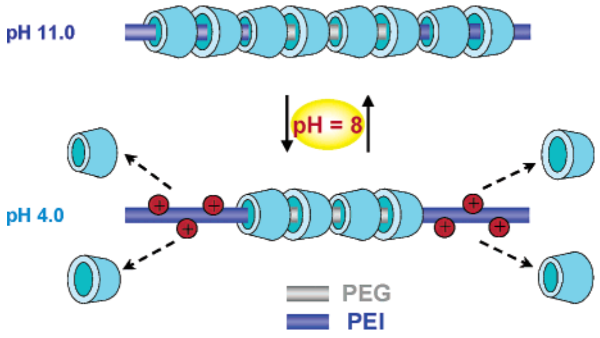


Figure 5. Schematic illustration for the block-selective polypseudorotaxane formation via pH variation.

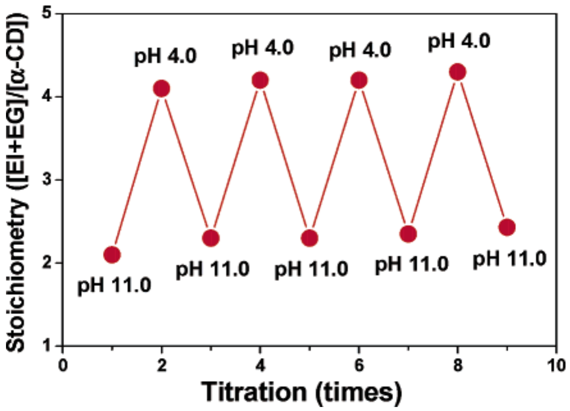


Figure 6. pH-dependent changes in stoichiometry between [EI + EG] and [α-CD].

complexation below pH 8.0 is ascribed only to the PEG block, the stoichiometry of [EG] to [α-CD] in the polypseudorotaxanes was found to be about 2:1 (Table 2), which matched well with the case of well-known PEG/α-CD polypseudorotaxanes.[2] In the case of $EI_{29}EG_{45}EI_{29}$/α-CD system, the same tendency was observed (data not shown). This result supports that α-CDs threaded on the PEI block at pH 11.0 are dethreaded by changing the pH below 8.0.

For the polypseudorotaxanes recovered at pH below 8.0, we noted that the stoichiometry was found to be about 2:1 even after 10 min equilibration at each pH, on the basis of the molar ratio of [EG]:[α-CD]. This indicates that, upon ionization of PEI, the α-CDs complexed formerly with the PEI block at pH 11.0 were expelled from the polymer chains in a fast mode, as shown in the schematic illustration of Figure 5.

Figure 6 shows that the dethreading/threading process of α-CDs onto the PEI block was reversibly controlled via pH variation. It is interesting to note that the consecutive change in pH from 4.0 to 11.0 or vice versa induced the reversible complexation of α-CDs with the PEI blocks. The dethreading at pH 4.0 leading to rapidly expelled water-soluble α-CDs and protonated PEI chain resulted in a decreased turbidity of the mixture. In this case, another α-CDs include in the PEG segments are remained as they were, which led the mixture to a somewhat turbid solution. In the meantime, once pH was dropped to pH 4.0, 100% recovery of the expelled CDs onto the deprotonated PEI chains was not observed even after returning to pH 11.0, but over 85% of CDs was reversibly threaded again onto the unionized PEI blocks, as estimated with the stoichiometry.

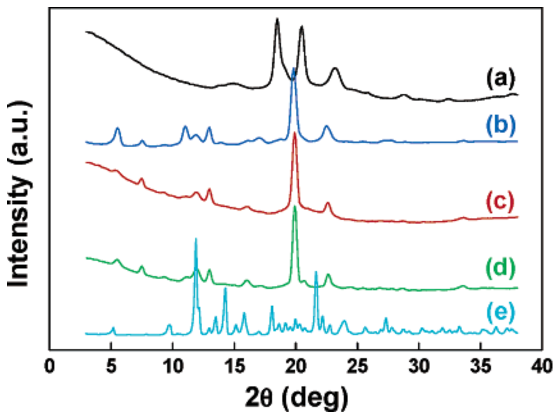


Figure 7. X-ray diffraction patterns of $EI_{22}EG_{45}EI_{22}$ (a), PEG (M_n 3400)/α-CD (b), $EI_{22}EG_{45}EI_{22}$/α-CD formed at pH 11.0 (c), and $EI_{22}EG_{45}EI_{22}$/α-CD formed at pH 4.0 (d), and α-CD (e).

Powder X-ray Diffraction Measurements. Figure 7 shows wide-angle X-ray diffraction patterns of the guest polymer $EI_{22}EG_{45}EI_{22}$, a PEG (M_n 3400)/α-CD polypseudorotaxane, $EI_{22}EG_{45}EI_{22}$/α-CD polypseudorotaxanes formed at pH 11.0 and pH 4.0, and the host α-CD, respectively. The triblock copolymer shows two peaks overlapped from both of PEI and PEG at 18.5 and 23.2°, and a characteristic peak only from crystalline PEI at 20.5° (Figure 7a).[11] The diffractograms of the $EI_{22}EG_{45}EI_{22}$/α-CD polypseudorotaxanes showed patterns quite different from those of the host α-CD and the guest $EI_{22}EG_{45}EI_{22}$. It is interesting to note that the characteristic peak of crystalline PEI at $2\theta = 20.5°$ completely disappears in the pattern of the polypseudorotaxane, which was formed at pH 11.0 (Figure 7c). This suggests that the polymer chains are completely shielded by α-CD molecules to show the reflections assignable only to the crystalline polypseudorotaxane structure. Besides, this observation was well supported by the 2:1 stoichiometry of [EI + EG]:[α-CD] for the polypseudorotaxanes. The profile of the $EI_{22}EG_{45}EI_{22}$/α-CD polypseudorotaxanes at pH 11.0 is almost the same as the typical pattern reported for the PEG/α-CD polypseudorotaxane (Figure 7b), where the strong peak at $2\theta = 20.0°$ ($d = 4.44$ Å) has been assigned to the 210 reflection of the hexagonal form with the lateral unit cell dimension $a = 13.6$ Å.[2,12] Besides, the patterns of $EI_{22}EG_{45}EI_{22}$/α-CD polypseudorotaxanes are in good accordance with those observed for channel-type polymer inclusion complexes,[2,13] indicating that $EI_{22}EG_{45}EI_{22}$ was inserted into α-CDs to form the channel-type crystalline polypseudorotaxanes.

The striking finding is that the polypseudorotaxane recovered from pH 4.0 exhibits the characteristic signal at $2\theta = 20.5°$, which is ascribed to crystalline PEI (Figure 7d). This proves that the decrease in pH induces the dethreading of α-CD molecules exclusively from the ionized PEI block, thereby resulting in the crystalline PEI structure showing up in the X-ray diffratogram.

Solid-State ^{13}C CP/MAS NMR Spectroscopy. The formation of inclusion complexes was confirmed in the

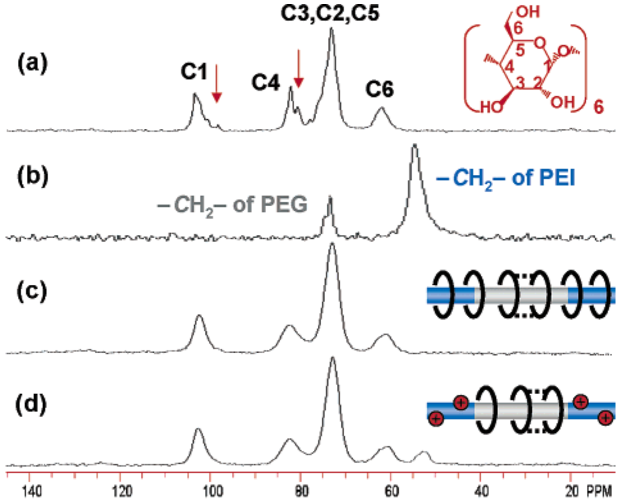


Figure 8. Solid-state ^{13}C CP/MAS NMR spectra of α-CD (a), $EI_{22}EG_{45}EI_{22}$ (b), $EI_{22}EG_{45}EI_{22}$/α-CD formed at pH 11.0 (c), and $EI_{22}EG_{45}EI_{22}$/α-CD formed at pH 4.0 (d).

solid state by ^{13}C CP/MAS NMR spectroscopy (Figure 8). Free α-CD assumes a less symmetrical conformation in the crystal state, where the C(1)−O−C(4) glycosidic linkage is distorted. The resonance signals appeared at 98 and 80 ppm in Figure 8a are assigned to C-1 and C-4 adjacent to conformationally strained glycosidic linkage of CDs, respectively. Besides, the spectrum of uncomplexed α-CD shows strong resolved splitting for C-1, C-4, and C-6, reflecting that α-CD molecules are in different environments with less symmetric cyclic conformation. For the pseudorotaxanes (Figure 8c,d), the signals of C-1, C-4, and C-6 from each glucose unit in α-CD show symmetric single peaks. This result indicates that, upon the inclusion of $EI_{22}EG_{45}EI_{22}$ into the cavity of α-CD, the conformational strain over the α-CD rings is greatly released to assume a symmetrical cyclic structure. Thus, it is suggested that $EI_{22}EG_{45}EI_{22}$ was inserted into α-CDs to form tunnel-structured inclusion complexes. We note that the resonance signal of PEI was not observed with the polypseudorotaxane formed at pH 11.0, whereas it was clearly observed with the polypseudorotaxane formed at pH 4.0. It can be suggested that the molecular motion of the polymer chains in the CD channel was greatly limited, and thus the whole polymer chains were complexed with CD molecules at pH 11.0. On the other hand, the pH decrease to pH 4.0 resulted in the pumping-out of CDs from the ionized PEI block, thereby leading to a fair of mobility of the PEI chains. This strongly supports the formation of the block-selective polypseudorotaxane by controlling the solution pH.

Conclusions

The unique pH-dependent polypseudorotaxane formation between α-CD and the triblock copolymer (PEI-*b*-PEG-*b*-PEI) was investigated. The results in this study strongly supported our assumption that the control of pH can induce the block-selective inclusion complexation to form the polypseudorotaxanes, where α-CDs could be threaded exclusively on the middle PEG block by controlling pH. It is suggested that the use of block copolymers with relevant polymeric combination can be an attractive approach rather than employing the homopolymer in designing polyrotaxane-based molecular pistons, where the location of cyclic CDs along the polymer chains can be switched to a specific segment in response to external stimuli.

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