

Polyurethane-Type Poly[3]rotaxanes Synthesized from Cyclodextrin-Based [3]Rotaxane Diol and Diisocyanates

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Synthesis of polyurethane-type poly[3]rotaxanes is achieved by polyaddition between a cyclodextrin (CD)-based [3]rotaxane diol and various diisocyanate species, which provide a more defined structure compared to conventional polyrotaxane syntheses. In this study, hydroxyl groups on CDs of [3]rotaxane diol are initially acetylated, and deprotected after the polyaddition to introduce polyurethane backbone structure into polyrotaxane framework. Despite a relatively complicated chemical structure, [3]rotaxane diol monomer is successfully synthesized in a high yield (overall 67%) without any taxing purification process, which is beneficial for practical applications. The polymerization itself proceeds well under a standard polyaddition reaction condition to afford corresponding polyurethanes around 80% yield with $M_n > 30$ kDa. The poly[3]rotaxanes show different aggregation behavior or optical properties, whether or not acetyl groups are present, and are analyzed by XRD, SEM, and fluorescence measurements.

blocks.^[1,2] One of the most famous phenomena in this regard is the toughening effect observed in polymer networks that are crosslinked by rotaxane framework, which is induced by stress distribution through movable crosslinking structure.^[3] Moreover, α -cyclodextrin (CD)-based polyrotaxane, typically derived from a linear polymer chain such as poly(ethylene glycol) (PEG) or poly(caprolactone) (PCL) with many CD rings on it, is known to form aggregation structures induced by the hydrogen bonding among CD units.^[4] To make most out of these unique phenomena, a fine control of the rotaxane structure is obviously the key, e.g., the number/directions of ring units or the polymer backbone. However, in general, a well-controlled rotaxane framework often requires a multistep synthesis/purification, limiting it for any materials application.^[1-4]

As a way around, the rotaxane framework is often constructed by a facile synthetic method with a rough structural control to enable a scalable synthesis.^[1-4] Especially when it comes to CD-based polyrotaxanes, the type of suitable polymer backbones is very regulated, limiting its potential as a material (Figure 1A). Therefore, the development of new methods to overcome this synthetic limitation is required.

In this regard, Akae, Takata, and co-workers developed an easy scalable synthesis of CD-based [3]rotaxane, which achieves a fine control of the rotaxane structure at the same time, and can be integrated into various polymers, such as polyester, vinyl polymers, and polyurea (Figure 1B).^[5-7] In their method, hydroxyl groups on CDs can be easily (de)protected by acetyl groups, and according to the degree of acetylation, the resulting [3]rotaxane framework exhibited aggregation structures and unique fluorescence from the axle end moieties, supporting its utilization as a functional building block for polymer materials. Overall, this molecular design enables further expansion of the synthetic tool kit of defined rotaxane framework to cover conventionally unaddressed material types. For example, polyurethane is one of the most produced materials in the world due to its highly tunable thermomechanical property and biocompatible nature.^[8,9] However, the direct introduction of polyurethane backbone in CD-based polyrotaxane framework has not been so easy, because the diisocyanate monomer required for polyurethane production could react with hydroxyl groups on CDs. Since the practical application of polyurethane is largely derived from its hydrogen bond formation, the material design by combining a polyurethane backbone with a CD-based polyrotaxane would be interesting to study the effect by multiple hydrogen bonds on the materials

1. Introduction

Rotaxane-based materials are known to show very different properties from conventional materials, which is induced by the unique mechanical bonding motif between the building

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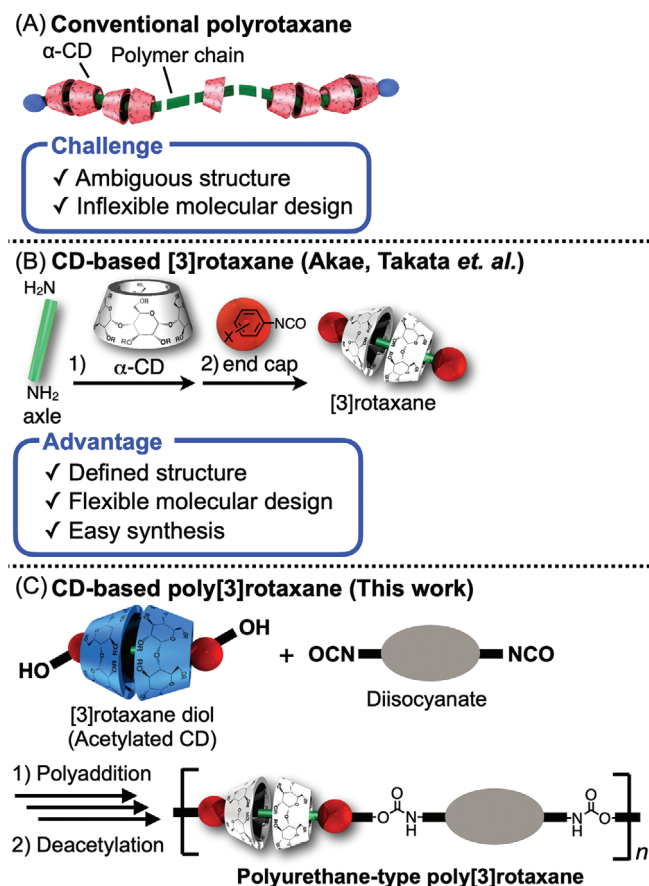


Figure 1. Schematic illustration of A) polyrotaxane (conventional study); B) CD-based [3]rotaxane; C) polyurethane-type poly[3]rotaxane (this work).

properties. Considering the above, in this study, we developed the synthesis of novel polyurethane-type poly[3]rotaxane featuring a defined structure by using [3]rotaxane as a building block, and evaluated their properties (Figure 1C). Polymers are synthesized by the polyaddition between CD-based [3]rotaxane diol and diisocyanate comonomers and successive deprotection of acetyl groups on CD units. Depending on the presence of the acetyl groups, poly[3]rotaxanes are expected to show different aggregation behavior or optical properties.

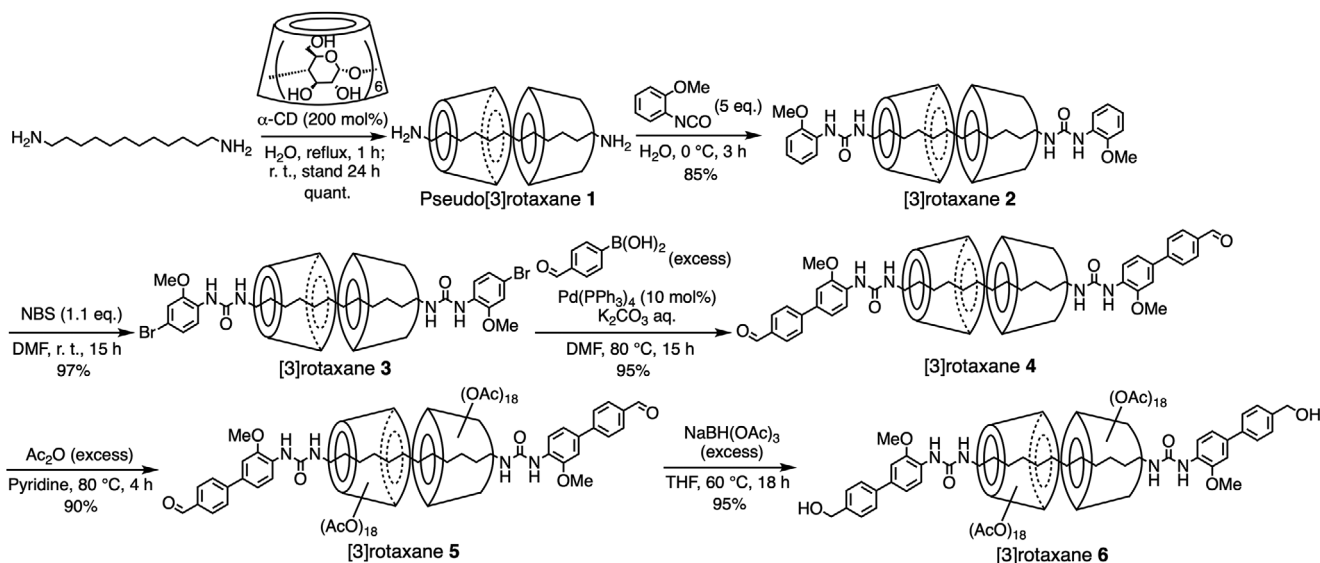
2. Results and Discussion

[3]Rotaxane diol **6** was synthesized by following previous reports (Scheme 1).^[5–7] First, the inclusion complex pseudo[3]rotaxane **1** was formed by mixing 1,12-diaminododecane and α -CD in water, and subsequent end-capping reaction by *o*-methoxy phenyl isocyanate afforded [3]rotaxane **2**. Here, the direction of two CD rings was fixed in a head-to-head manner owing to the hydrogen bonding between two CD units, providing a defined rotaxane structure. Moreover, this rotaxation step was successfully conducted in a 100 g scale in a 1 L flask in high yield (85%), supporting its applicability on the large-scale synthesis for material application. Afterwards, (1) bromination on axle ends (97% yield), (2) Suzuki coupling reaction on the aromatic bromine substituent (95% yield), (3) acetylation of hydroxyl groups on CDs

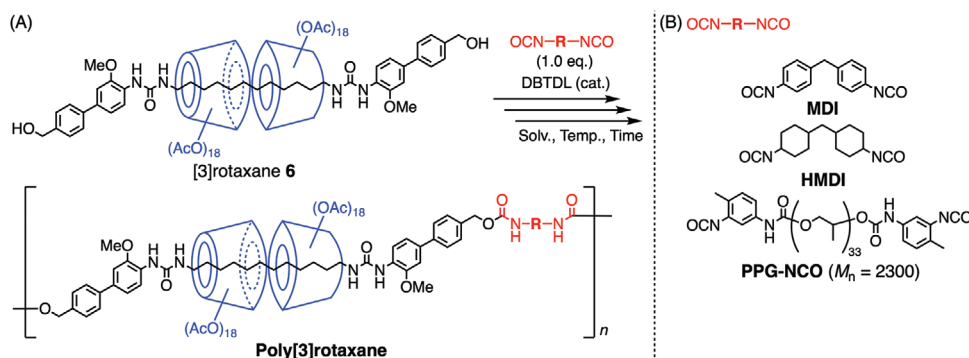
(90% yield), and (4) reduction of the aldehyde groups on the axle ends to alcohol (95% yield) successfully provided [3]rotaxane diol **6**. Notably, all the synthetic steps do not require any demanding purification processes, which is typically required for defined rotaxane structure syntheses.^[1–4] Purification was conducted by simple precipitation or washing treatment, supporting the easy monomer production in this method. Overall yield here was 67% from α -CD to [3]rotaxane **6**. It means that when 10 g of α -CD was used, 14 g of [3]rotaxane **6** were obtained, which is significantly high overall yield compared with other defined rotaxane species.^[1–4] As reported previously, derivatives of the [3]rotaxane diol can be easily synthesized by using other phenyl isocyanate end-caps or Suzuki-coupling reagents, enabling the fine tuning of resulting polymer structure.^[5–7]

Next, polyaddition reaction between [3]rotaxane diol **6** and multiple diisocyanate comonomers were conducted to synthesize polyurethane type poly[3]rotaxane (Scheme 2, Table 1). First, methylenediphenyl 4,4'-diisocyanate (MDI) was used as a comonomer in a standard reaction condition as it is one of the most popular diisocyanate monomers in polyurethane synthesis.^[8] Namely, both comonomers were reacted in CH_2Cl_2 (0.50 M) in the presence of the catalyst dibutyl tindilaurate (DBTDL) at room temperature for 1 h, and purified by the precipitation in MeOH (Table 1, PU1). The obtained product did not completely dissolve in common organic solvents such as THF, DMSO, and DMF, which was a disadvantage of the further processing of the polymer and spectroscopic analysis. In a rough estimation, around 80% of the product dissolved in DMAC or CHCl_3 , hence, the soluble fraction was analyzed by ^1H NMR and SEC spectra, and clearly proved the production of the desired product (Figure 2). In the ^1H NMR spectrum after polyaddition, a urethane NH signal was observed at around 6.6 ppm, the signal of benzyl ϵ proton shifted from 4.6 ppm to around 5.1 ppm, and aromatic signals became broader, which were all a consequence of the polyurethane formation. Although the soluble part was proven to be a desired polyurethane-type poly[3]rotaxane PU1, the analysis should be conducted not only on the soluble part, but also on the insoluble part for getting deeper understanding of this synthesis. Thus, we did not carry out further detailed analysis on it, and moved on to the synthesis of more soluble polymers. The low solubility of PU1 was probably caused by the high rigidity of the MDI segment, suggesting the use of more flexible linker would increase the solubility of the product.

Based on this hypothesis, 4,4'-methylenebis(cyclohexyl isocyanate) (HMDI, hydrogenated MDI) was used as a more flexible linker than MDI (Scheme 2, Table 1, PU2–PU6). As a result, employing HMDI afforded a soluble polyurethane-type poly[3]rotaxane in good yield, which was undoubtedly characterized by ^1H NMR and SEC analysis (Figure 3). These HMDI-based polymers were fully soluble in DMAC or CHCl_3 , which showed a clear difference from the MDI-based one. Meanwhile, a short reaction time with HMDI resulted in a lower conversion of the comonomers (Table 1, PU2), clearly detected by ^1H NMR and SEC analyses. Therefore, an overnight reaction was required to reach full conversion, obviously caused by a lower reactivity of the aliphatic isocyanate on HMDI than the aromatic one on MDI. Here, the reaction time for 24 and 48 h (Table 1, PU3 and PU4) did not significantly increase the molecular weight of the polymers, suggesting 24 h was a sufficient reaction time. To reach a



Scheme 1. Synthesis route for [3]rotaxane 6.



Scheme 2. A) Synthesis of poly[3]rotaxane; B) chemical structures of diisocyanate comonomers.

high conversion within a short reaction time, the polymerization was conducted at a higher temperature (60 °C) in CHCl_3 (Table 1, PU5 and PU6). As a result, higher molecular weights were obtained for polymers synthesized at higher temperatures; however, with broader molecular weight distributions and in lower

yields, likely due to undesired side reactions. Since the reaction at room temperature for 24 h (PU3) already afforded sufficiently high molecular weight ($M_n = 31$ kDa) in high yield (85%), this reaction condition could be considered as a sufficiently optimized condition so far. Herein, the polyaddition between [3]rotaxane

Table 1. Polyaddition between [3]rotaxane 6 and diisocyanates (Scheme 2).

Polymer	Monomer	Time [h]	Conv. ^{a)} [%]	Yield [%]	$M_n^b)$ [kDa]	$M_w^b)$ [kDa]	$\mathcal{D}^b)$
PU1	MDI	1	>99	78	31 ^{c)}	50 ^{c)}	1.6 ^{c)}
PU2	HMDI	1	48	85	6.8	8.2	1.2
PU3	HMDI	24	>99	85	31	45	1.4
PU4	HMDI	48	>99	91	36	55	1.5
PU5 ^{d)}	HMDI	1	>99	67	30	54	1.8
PU6 ^{d)}	HMDI	24	>99	63	64	150	2.4
PU7	PPG-NCO	1	34	74	14	16	1.2
PU8	PPG-NCO	2	44	78	15	18	1.2
PU9	PPG-NCO	24	>99	81	37	68	1.9

^{a)} Calculated by $^1\text{H NMR}$; ^{b)} Calculated by SEC (eluent; DMAc, flow rate; 0.5 mL min^{-1} , 50 °C, polystyrene standard); ^{c)} Only DMAc soluble part; ^{d)} Reaction was conducted in CHCl_3 at 60 °C.

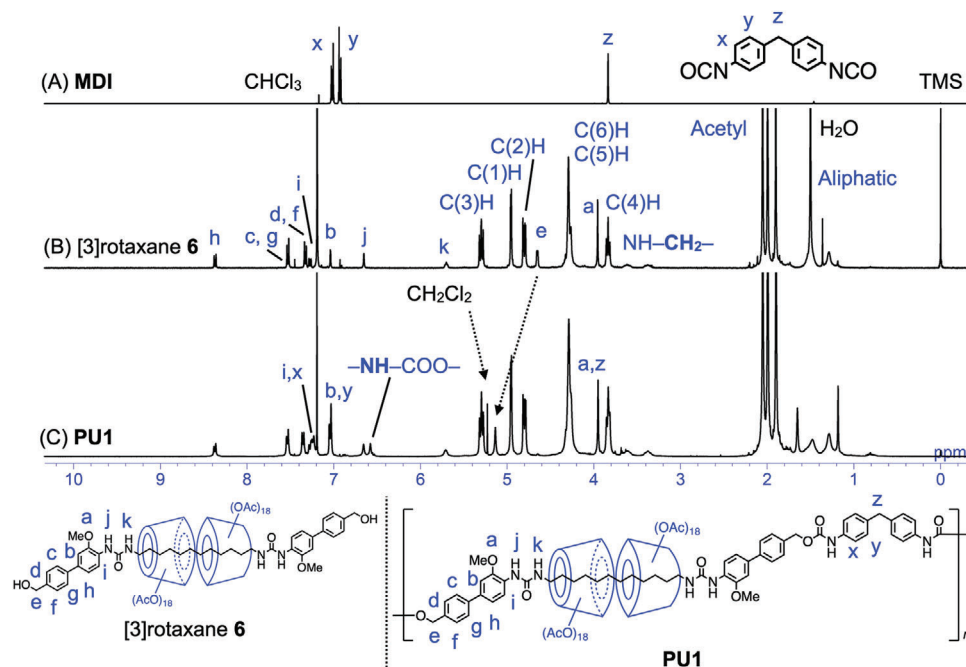


Figure 2. ^1H NMR spectra of A) MDI; B) [3]rotaxane **6**; C) PU1 (400 MHz, CDCl_3 , 298 K).

diol **6** and HMDI was proved to provide expected poly[3]rotaxane in high yield with high solubility, suggesting the successful synthesis of the polyurethane-type poly[3]rotaxane having defined structure.

To introduce another flexible linker to poly[3]rotaxane framework, PPG-NCO was used as a diisocyanate (macro)comonomer instead of HMDI (Scheme 2, Table 1, PU7–PU9). As a result, the reaction also successfully afforded the corresponding poly[3]rotaxane similar to the case of HMDI. In this case, the reactivity of the aromatic isocyanate on PPG-NCO must be higher than the aliphatic ones on HMDI, but a methyl substituent next to itself and a long poly(propylene glycol) (PPG) linker structure may reduce its reactivity, which could have resulted in a

slower polyaddition reaction than MDI. Since isocyanate end-functionalized polymers can be easily synthesized as reported previously,^[9] various polymer linker structures could be flexibly introduced in polyurethane-type poly[3]rotaxane framework by this synthetic method.

Next, the deacetylation of poly[3]rotaxanes was carried out to generate hydroxyl groups on CD units (Scheme 3). For that, HMDI-based PU10 and PPG-NCO-based PU11 were prepared as substrate polymers by Scheme 2. To avoid damaging polyurethane backbone structure, a mild reaction condition was applied for the hydrolysis.^[7] Namely, an excess of K_2CO_3 aq. was added to the solution of PU10 in DMF/EtOH mixed solvent, and the reaction was carried out at room temperature for two days. As a result, 89% deacetylated product PU10_Ac11 (named as 11% acetylated sample) was obtained (Scheme 3A), with the deacetylation ratio was calculated by ^1H NMR (Figure 4). Moreover, the SEC profiles of the polymers before and after the deacetylation showed almost the same patterns, suggesting the polyurethane backbone structure was not damaged during the hydrolysis (Figure 5). To achieve a higher deacetylation degree, harsher reaction condition would be required, such as higher reaction temperature. However, such hydrolysis condition could damage polyurethane backbone or rotaxane structure.^[5,6] Since a high degree (89%) deacetylated product was already obtained, further optimization of the deacetylation was not carried out so far. Similarly, PU11 was also deacetylated (Scheme 3B). As a result, only 35% deacetylated product PU11_Ac65 (named as 65% acetylated sample) was obtained, which showed a much lower deacetylation ratio than PU10_Ac11. The reason of this difference was not clear, but could be speculated as follows. In case of HMDI linked polyurethane, the distance between neighboring rotaxane units is much closer than that of PPG-NCO linked rotaxane, inducing the promotion of hydrolysis on the former

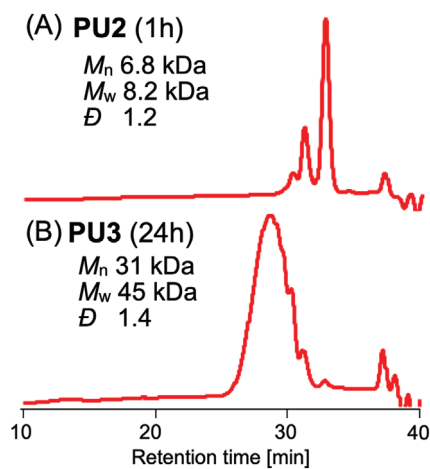
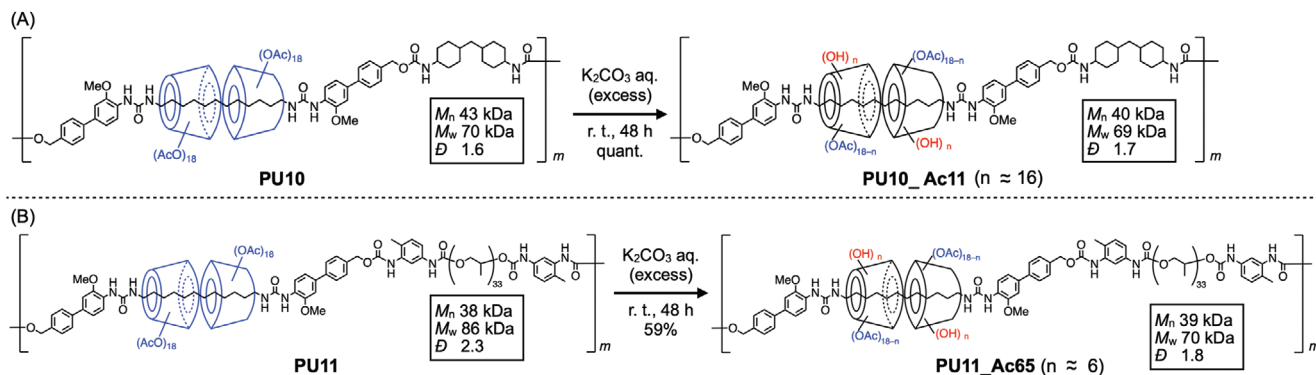


Figure 3. SEC profiles of A) PU2; B) PU3 (eluent; DMAc; flow rate: 0.5 mL min^{-1} ; detected by RI).



Scheme 3. Deacetylation of A) PU10; B) PU11.

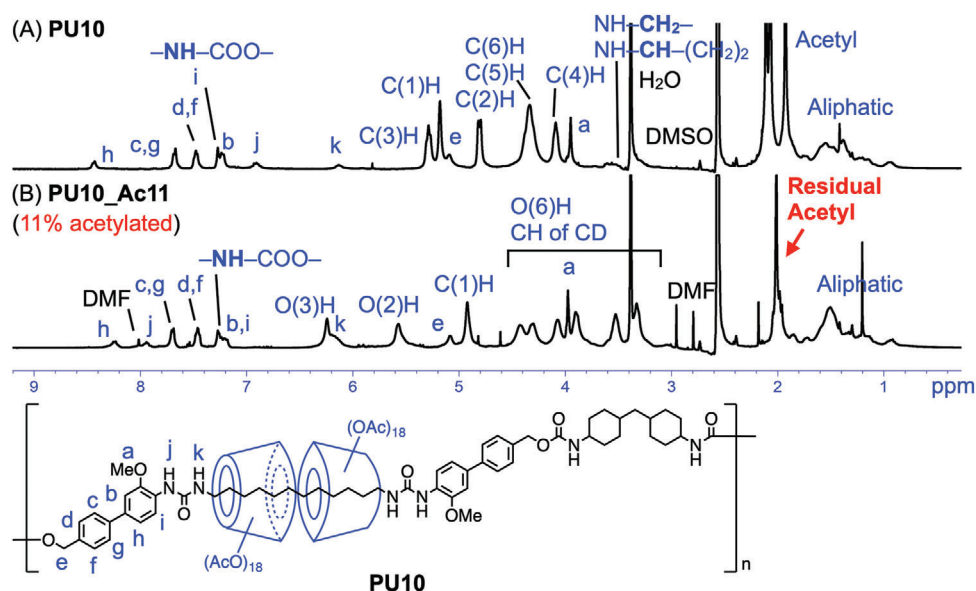


Figure 4. 1H NMR spectra of A) PU10; B) PU10_Ac11 (400 MHz, DMSO- d_6 , 298 K).

by the hydroxyl groups on CDs derived from deacetylation, i.e., as a neighboring effect. This promotion of the hydrolysis could hardly act in the PPG-NCO linked polyurethane, since a long flex-

ible PPG linker would behave as a large steric hindrance. Even though a full conversion of the deacetylation was not achieved so far, mostly deacetylated polyurethane-type poly[3]rotaxane was successfully synthesized via the acetyl protection on CD units. As demonstrated here, (de)acetylation of CD units could effectively expand the accessible polymer framework exhibiting CD-based rotaxane structure.

As previously studied, the aggregation formation by partially acetylated CD-based [3]rotaxane could work effectively in proportion to the existence of hydroxyl groups.^[7] Hence, the aggregation behavior of PU10_Ac11 was also studied. By following previous reports,^[4]–n,7] PU10_Ac11 was dispersed in H₂O or THF to induce aggregation, and the precipitate was collected by filtration. The obtained samples were evaluated by powder XRD and SEM (Figure 6). XRD profiles showed broad patterns with local maximums around $2\theta = 20^\circ$. Compared with the sharper XRD patterns typically observed in the hexagonal packing type aggregate,^[4]–n,7] obviously PU10_Ac11 did not form the expected aggregation structure. However, compared with the XRD profile of PU10 (Figure 6A), which contained perfectly acetylated CDs on it, those of PU10_Ac11 were sharper (Figure 6B,C). Also,

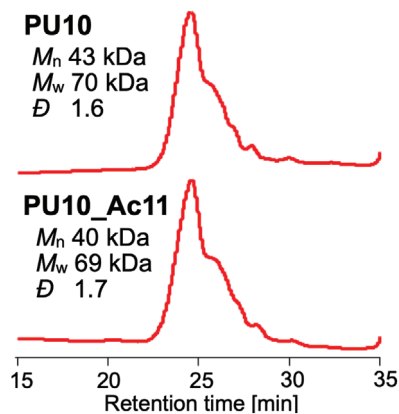


Figure 5. SEC profiles of A) PU10; B) PU10_Ac11 (eluent; DMAc; flow rate: 0.5 mL min⁻¹; detected by RI).

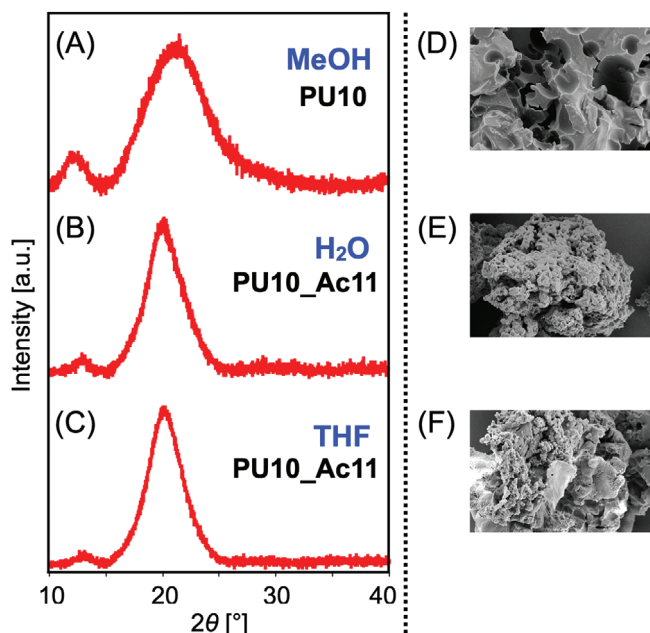


Figure 6. Powder XRD profiles of A) PU10 treated by MeOH; B) PU10_Ac11 treated by H₂O; C) PU10_Ac11 treated by THF. SEM images (x5000) of D) PU10 treated by MeOH; E) PU10_Ac11 treated by H₂O; F) PU10_Ac11 treated by THF.

when the peak top around $2\theta = 20^\circ$ was more carefully compared, that of PU10 was around 21.5° , while those of PU10_Ac11 were around 19.6° . Those values were consistent with the previous report; the former was derived from the amorphous halo of acetylated [3]rotaxane, while the latter were assigned as the signal from (210) plane of the hexagonal unit cell parameters $a = b = 13.65 \text{ \AA}$ and $c = 16.4 \text{ \AA}$, as the head-to-head and tail-to-tail repeating inclusion structure.^[4-n,7] Moreover, SEM images of those samples showed a clear difference, with a smoother surface on PU10 (Figure 6D) than PU10_Ac11 (Figure 6E,F). Considering the above, PU10_Ac11 did not form a clear aggregation structure compared with single [3]rotaxane molecule, but its morphology was obviously changed from PU10 by the deacetylation, probably because the former had more ordered structure by the hydroxyl groups on CD units. In case of CD-based [3]rotaxane species without polymer backbone, the aggregate formation was clearly observed,^[7] suggesting the induction of the aggregation may not have worked effectively in polyurethane-type poly[3]rotaxane framework. The reason of this was not clear, but in the polymer, the rotaxane unit could not freely locate as is the case for single [3]rotaxane molecule, which made the aggregate formation more difficult. Considering more flexible placement of [3]rotaxane units, more flexible linker or bond type other than urethane may promote the aggregate formation more effectively. Here, although the clear aggregate formation was not observed on the deacetylated samples, the morphological difference was detected between before and after the deacetylation.

Next, the fluorescence behavior of poly[3]rotaxanes was studied. As previously reported, deacetylation of [3]rotaxane 5 to 4 (chemical structures are displayed on Scheme 1) induced the red shift of the emission spectra derived from biphenyl groups

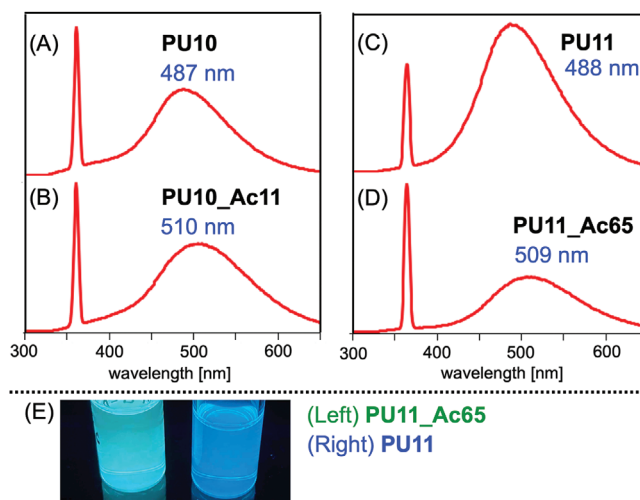


Figure 7. Fluorescence spectra of A) PU10; B) PU10_Ac11; C) PU11; D) PU11_Ac65 ($100 \times 10^{-6} \text{ M}$ of the repeating unit, DMF, 298 K, $\lambda_{\text{ex}} = 360 \text{ nm}$). E) Photos of (left) PU11_Ac65; (right) PU11 (DMF, under dark irradiated by 365 nm light).

on the axle ends.^[5b] This red shift was caused by the change of the solvation from hydrophobic acetylated CD units exhibiting 36 acetylated hydroxyl groups to hydrophilic native CDs with 36 hydroxyl groups. Since the biphenyl groups on [3]rotaxane 4 and 5 showing push-pull type electron transfer by the methoxy and aldehyde substituents, such a solvation change highly affects the emission wavelength like a solvatochromism.^[5b,10] In case of [3]rotaxane 6, the aldehyde substituents on [3]rotaxane 5 become alcohol groups, weakening this solvatochromism nature and fluorescence intensity itself. However, a noticeable change of the fluorescence wavelength after the deacetylation was already recognized by naked eyes. Therefore, fluorescence spectra were measured on poly[3]rotaxane samples to evaluate it in more detail (Figure 7) (see Supporting Information). All acetylated samples, [3]rotaxane 6, PU10, and PU11 showed similar UV-vis absorption and fluorescence spectra exhibiting emission peaks at around 490 nm when excited by 360 nm light. Meanwhile, deacetylated poly[3]rotaxanes PU10_Ac11 and PU11_Ac65 showed around 20 nm red shifted emission spectra. Such a red shift by deacetylation was consistent with the results of the previous study on [3]rotaxane 5 to 4,^[5b] meaning that the solvation effect observed in small molecule samples also took place in polymers. As shown on the photos, the fluorescence color difference was clearly detected by naked eyes (Figure 7E). Considering the above, deacetylation on poly[3]rotaxanes certainly induced the polarity change on the [3]rotaxane segment as detected by the fluorescence difference.

3. Conclusion

Polyurethane-type poly[3]rotaxanes were successfully synthesized by the polyaddition of acetylated CD-based [3]rotaxane diol and diisocyanates, and subsequent hydrolysis under mild reaction condition. This (de)acetylation protocol could effectively and versatily expand the molecular design of polymers exhibiting CD-based rotaxane structure. Depending on the existence of

acetyl groups on CD units, morphology of the poly[3]rotaxane changed a lot as evaluated by aggregation and fluorescence study. Moreover, it was implied that the aggregation induction requires more optimal condition than the fluorescence color change, although both characteristics are in principle triggered by the same deacetylation. This is probably because the aggregation is intermolecular interaction, while the fluorescence is intramolecular phenomenon/effect. Since this synthetic method is easy and scalable compared with conventional synthesis of rotaxanes having defined structures, its material application and further study are currently ongoing in our group by using [3]rotaxane as a functional building block of polymer architectures.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

cyclodextrins, polyaddition, polyurethane, precise polymer synthesis, rotaxanes

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