Polypseudorotaxanes Constructed from Pillar[5]arenes and Polyamides by Interfacial Polymerization

COMMUNICATION

Polypseudorotaxanes Constructed from Pillar[5]arenes and Polyamides by Interfacial Polymerization

Tomoki Ogoshi,*[a,b] Miyu Yoshiki,[c] Takahiro Kakuta,[b,c] Tada-aki Yamagishi,[c] and Motohiro Mizuno[c]

Polypseudorotaxaenes constructed from pillar[5]arene rings and polyamide chains were successfully synthesized by interfacial polymerization between diamines and dicarbonyl chlorides in the presence of pillar[5]arene. The dicarbonyl chloride length and the assocation constants of dicarbonyl chloride-pillar[5]arene complexes were important factors in producing polypseudorotaxanes with high cover ratio of pillar[5]arene rings.

Polyamides are important engineering plastics owing to their high form stability and high melting points.[1-3] These properties are due to strong intermolecular hydrogen bonds between amide groups in the polymer chains. However, owing to these strong hydrogen bonds, polyamides are insoluble in most common solvents, except for extremely harsh conditions such as strong acids and LiCl in NMP or DMF, which can cut intermolecular hydrogen bonds between polymeric chains to dissolve polyamides.

Polypseudorotaxanes, in which many macrocyclic components are threaded onto polymeric chains, have attracted much attention because the cyclic components move and rotate freely on the polymeric chain.[4-8] Polypseudorotaxanes constructed from polyamides and macrocyclic hosts such as cyclodextrins,[9-12] cucurbit[n]urils[13] and crown ethers[14] have been synthesized, but a serious problem in the preparation of polyamide-based polypseudorotaxanes is their extremely low solubility. Accordingly, there are limited reported examples of polyamide-based polypseudorotaxanes.[9-14] Simple approaches to produce polypseudorotaxanes involve the polycondensation
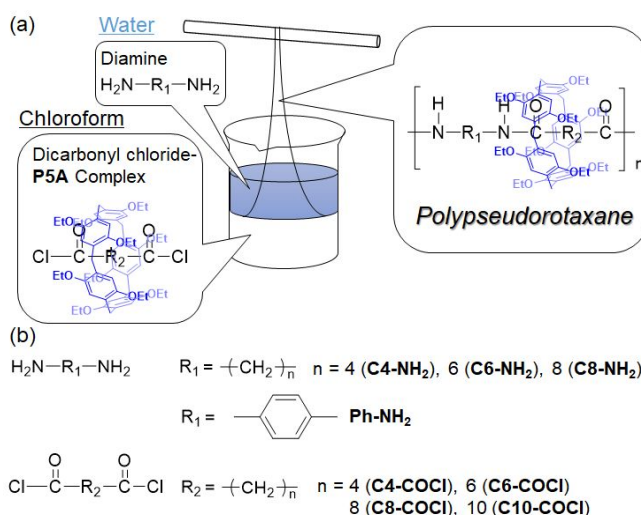

Fig. 1 (a) Polypseudorotaxane synthesis by interfacial polymerization between diamine and dicarbonyl chloride in the presence of pillar[5]arenes. (b) Chemical structures of monomers used for the interfacial polymerization.

of monomers in the presence of macrocyclic compounds or pseudorotaxanation between polyamides and macrocyclic compounds in good solvents for polyamides, such as strong acids and LiCl in NMP.[11-14] However, these conditions necessary to solubilize polyamides are harsh. Another approach is solid state complexation and polycondensation. Wenz and co-workers reported the solid-state thermal polycondensation of host-guest complexes between cyclodextrins and reactive α,ω-amino acid monomers. Heating the host-guest complex crystals under reduced pressure induced polycondensation, affording polypseudorotaxanes constructed from cyclodextrins and polyamides.[9, 10]

In this study, we successfully synthesized polyamide-based polypseudorotaxanes based on pillar[5]arenes. Pillar[n]arenes, which were first reported by our group in 2008,[15] are unique cylindrical-shaped macrocyclic molecules.[16-21] Owing to their electron-rich cavity, these compounds exhibit excellent host–guest properties to form complexes with neutral molecules,

[a.] Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan
[b.] WPI Nano Life Science Institute (WPI-NanoLSI), Kanazawa University Kakuma-machi, Kanazawa, Ishikawa, 920-1192, Japan
[c.] Graduate School of Natural Science and Technology, Kanazawa University Kakuma-machi, Kanazawa, Ishikawa, 920-1192, Japan
† Footnotes relating to the title and/or authors should appear here.
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including simple alkanes, *via* multiple CH–π interactions in chloroform.[19] Polyamides can be prepared by mild interfacial polycondensation between linear alkanes with carbonyl chloride termini in halogenated solvent and amines in aqueous solution. Therefore, in this study, the interfacial polycondensation of host-guest complexes between linear alkanes with carbonyl chloride termini and pillar[5]arene with 10 ethoxy groups **P5A** in chloroform and diamines in aqueous media (Fig. 1) was examined. By choosing the suitable monomers and feed ratios, we successfully synthesised polyamide-based polypseudorotaxanes highly covered with pillar[5]arene rings by interfacial polycondensation.

First, we investigated host-guest complexation between **P5A** and dicarbonyl chlorides with various alkyl chains. **P5A** formed 1:1 host-guest complexes with the linear alkane moieties of dicarbonyl chlorides in CDCl$_3$, as confirmed by ^{1}H NMR titrations (ESI, **Figs. S1**-**S4**). **C4-COCl** was first selected as the dicarbonyl chloride for preparing polypseudorotaxanes because the association constant (K) between **P5A** and **C4-COCl** determined by ^{1}H NMR titration was highest [K = (6.2 ± 0.09) × 10^4 M^{-1}] among dicarbonyl chlorides with **C4**, **C6**, **C8**, and **C10** linear chains (ESI). **C4** was a suitable length for the height of **P5A**, allowing the formation of stable host-guest complexes, in agreement with previous reports.[22-24] Therefore, **C4-COCl** was mixed with **P5A** in chloroform to form host-guest complexes. Hexamethylenediamine (**C6-NH$_2$**) was used as the diamine. An aqueous solution of the diamine was slowly added to a chloroform solution of the host-guest complexes at room temperature. After 1 h, a film was formed at the interface between chloroform and water. This film was pulled continuously from the interface in an unstirred reaction, forming ropes of polymeric film. To remove salts and unreacted dicarbonyl chloride and diamine, the polymer film was washed with hot water and methanol. To remove un-complexed **P5A**, the film was washed with chloroform, in which **P5A** is highly soluble. When small amounts of **P5A** (0.1, 0.3, and 0.5 equiv. relative to **C4-COCl**) were used, the polymeric film was obtained (**Table 1**, entries 1-3). However, the coverage ratios (number of nylon units covered by one **P5A** molecule) were 15 units/ring at maximum. No film formation was observed when 1 equiv. of **P5A** was used (entry 4), indicating that complexation inhibited the polycondensation. The axle length of **C4-COCl** was approx. 8.0 Å (Fig 2a), which was shorter than the height of **P5A** (approx. 10 Å). Therefore, the reactivity of the carbonyl chloride termini of **C4-COCl** with the amine termini of **C6-NH$_2$** was inhibited by **P5A** covering the reactive carbonyl chloride ends (Fig 2b). The inhibition of end-group reactivity was also observed in the synthesis of pillar[5]arene-based [2]rotaxanes.[25] To solve this problem, carbonyl chlorides with long linear alkyl chains were used. When 1 equiv. of **P5A** was used, polypseudorotaxanes were formed by **C6-**, **C8-**, and **C10-COCl** (entries 5-7). The cover ratio was 33 units/ring when **C6-COCl** was used (entry 5). The cover ratio increased to 22 units/ring for **C8-COCl**, (entry 6) and decreased again for **C10-COCl** (entry 7). The length of **C6-COCl** was approx. 10.3 Å, which was similar to the height of **P5A** (approx. 10 Å). Therefore, the length of **C6-COCl** remained short, such that coverage of the reactive carbonyl chloride ends

Table 1. Synthesis of polypseudorotaxanes *via* interfacial polymerization using linear dicarbonyl chlorides (**Cn-COCl**)^a

Entry	Cn-COCl	P5A (Equiv. to Cn-COCl)	Cover Ratio (number of units covered by one P5A ring)^c
1	**C4-COCl**	0.1	55
2	**C4-COCl**	0.3	18
3	**C4-COCl**	0.5	15
4	**C4-COCl**	1	-
5	**C6-COCl**	1	33
6	**C8-COCl**	1	22
7	**C10-COCl**	1	55
8	**C8-COCl**	4	3.2
9	**C8-COCl**	10	2.8
10	**C8-COCl**	12	5.8
11^b	**C8-COCl**	10	20

^{a}1 equiv. of **C6-NH$_2$** relative to **Cn-COCl** was used as the diamine. ^{b}In the presence of 4 equiv. of 1,4-dicyanobutane. ^{c}Cover ratios (number of nylon units covered by one **P5A** molecule) were determined by elemental analysis.
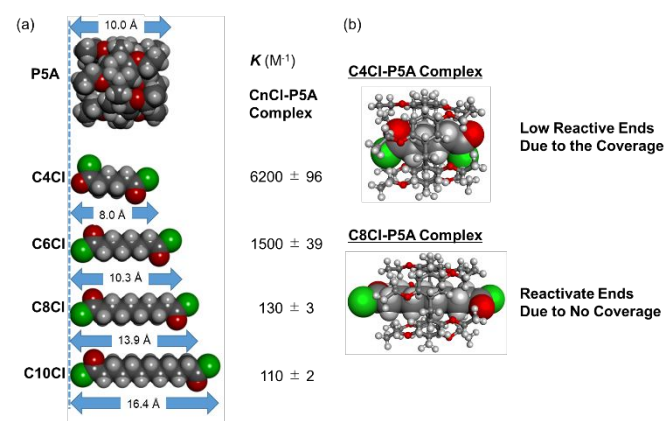

Fig. 2 (a) Dicarbonyl chloride monomer lengths, **P5A** height, and association constants (K) of the complexes. (b) Complexation-dependent reactivity of the carbonyl chloride ends.

inhibited polycondensation. The length of **C8-COCl** (approx. 13.9 Å) was greater than the height of **P5A**, such that uncovered carbonyl chloride ends were able to react with diamines to produce polymers (Fig. 2b). **C10-COCl** also had an alkyl chain length sufficient for condensation (approx. 16.4 Å), but the association constants (K) decreased with increasing alkyl chain length from **C4-COCl** to **C10-COCl**. The same trends were observed in linear-shaped guest molecules.[26] Therefore, to balance the dicarbonyl chloride length and the association constants (K), the highest cover ratio was obtained when **C8-COCl** was used as a monomer. To form polypseudorotaxanes with high cover ratios using **C8-COCl**, the amount of **P5A** was optimized. Cover ratios of 3.2 and 2.8 units/ring were obtained when 4 and 10 equiv. of **P5A** (relative to **C8-COCl**) were used, respectively (entries 8 and 9). The length of **C8-COCl** is sufficient to react with diamines to produce polymers even by complexation with **P5A**, therefore we successfully obtained polypseudorotaxanes with high cover ratios in the presence of excess amounts of **P5A**. Overall, polypseudorotaxanes with high cover ratios were successfully synthesized using **C8-COCl** and 4 or 10 equiv. of **P5A**. **P5A** forms stable host-guest complexes
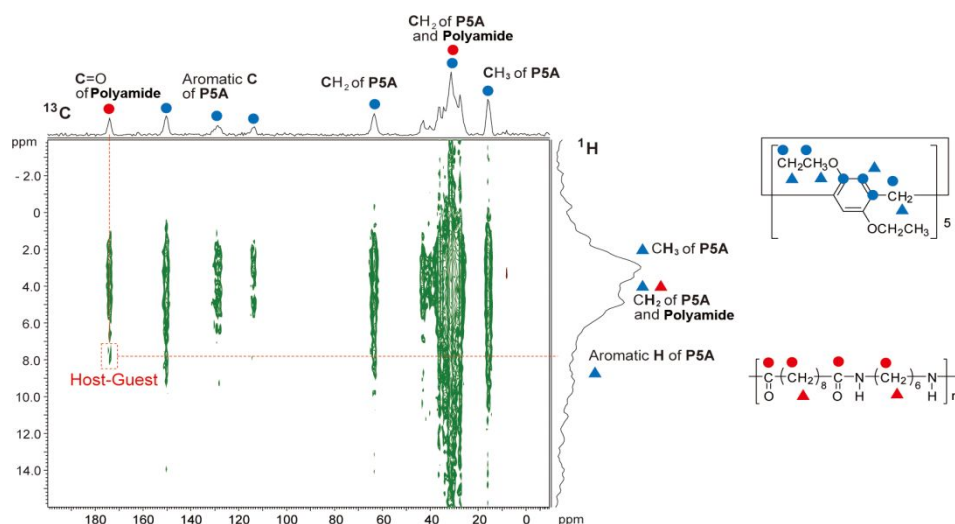
Fig. 3 Magnetic angle spinning 2D heterocorrelated NMR spectrum of polypseudorotaxane (entry 8) with PMLG homonuclear decoupling (ct = 2 ms).

with 1,4-dicyanobutane ($K > 10^4$ M^{-1}),[26] which is higher than dicarbonyl chlorides. To gain insight into the polypseudorotaxanation, the polypseudorotaxane was prepared in the presence of 1,4-dicyanobutane as a competitive guest. In the presence of 1,4-dicyanobutane, the cover ratio changed from 3.2 to 20 units/ring (entry 11), indicating that complexation between 1,4-dicyanobutane and **P5A** prevented polypseudorotaxane formation. This result also supported the formation of polypseudorotaxanes. The sample was not soluble in typical common solvents owing to low solubility of polyamides. Therefore, to confirm polypseudorotaxane formation, the polypseudorotaxane product (entry 8) was subjected to solid-state 2D $^1H/^{13}C$ hetero-correlated NMR spectroscopy with magic angle spinning (**Fig. 3**). We clearly found carbon signals from **P5A** (blue circles) and polyamide (red circles), indicating that the product was consisting of **P5A** and polyamide. The composition of the polypseudorotaxane was also confirmed by FT-IR measurements (**Fig. S6**). Cross-peaks were observed between the aromatic proton signals of **P5A** at about 8 ppm and the polyamide C=O carbon signals at 173 ppm, which were not observed in **P5A** and the polyamide (**Fig. S5**). These host-guest intermolecular cross-peaks clearly indicated the formation of a polypseudorotaxane structure in the solid state. To investigate the assembled structure of the polypseudorotaxane in the solid state, WAXS measurements were performed (**Fig. S7**). No clear difference was observed between the polyamide and polypseudorotaxane, indicating that hydrogen bonding networks remained in the polypseudorotaxane structure. No peaks from **P5A** were also observed in polypseudorotaxane, indicating that assembled structures of **P5A** in the solid state were completely different from the bulk assembled structures of **P5A**. The effect of threading with **P5A** on the thermal properties of the polyamide was investigated by DSC (**Fig. S8**). The polypseudorotaxane showed an endothermic peak at 212 °C in the heating process

and an exothermic peak at 180 °C. Similar endo- and exothermic peaks were observed in the polyamide (without **P5A**), indicating that the hydrogen bonding network was retained even after polypseudorotaxanation. However, an endothermic peak at 156 °C from **P5A** completely disappeared in the polypseudorotaxane, indicating that the assembled structures of **P5A** in the solid state were completely different from the bulk assembled structures of **P5A**, which was consist with the PXRD results.

Polypseudorotaxanes were also synthesized using other diamines instead of **C6-NH₂** (ESI). Polypseudorotaxanes were successfully obtained using diamines with different alkyl chains (**C4-NH₂**, **C8-NH₂**) and phenyl groups (**Ph-NH₂**).

In conclusion, we have successfully synthesized polypseudorotaxanes from pillar[n]arene rings and polyamide chains using interfacial polymerization. The dicarbonyl chloride monomer length and the association constants of the dicarbonyl chloride monomer-pillar[5]arene complexes were important factors in producing polypseudorotaxanes with a high cover ratio of pillar[5]arene rings. As interfacial polymerization did not require harsh conditions, the polyamide-based polypseudorotaxanes reported in this study are easy-to-fabricate. Although there are some reports of pillar[n]arene-based poly(pseudo)rotaxanes,[27-39] the present study represents the first example of polypseudorotaxanes constructed from pillar[n]arenes and polyamides. By utilizing the functionalization of pillar[n]arenes instead of pillar[n]arenes bearing ethoxy groups, the production of functionalized polyamide-based polypseudorotaxanes is now possible. This work is now under investigation in our laboratory.

Conflicts of interest

There are no conflicts to declare.

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