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Macromolecular [2]Rotaxanes: Effective Synthesis and Characterization

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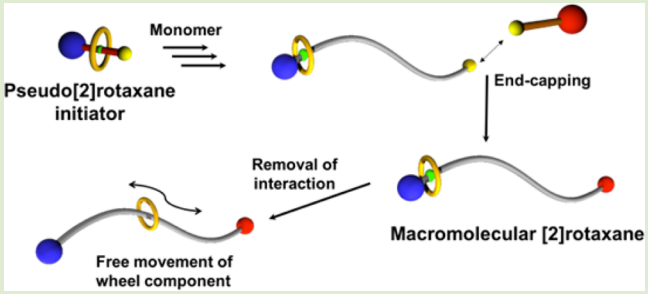
Supporting Information

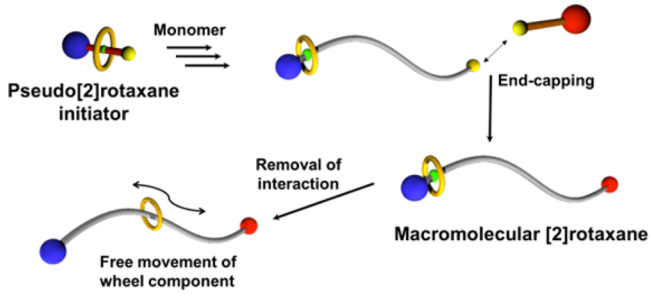
ABSTRACT: Macromolecular [2]rotaxanes, which consist of a polymer chain threading into a wheel component, were synthesized in high yield and with high purity. The synthesis was achieved by the ring-opening polymerization (ROP) of δ-valerolactone (VL) using a hydroxyl-terminated pseudorotaxane as an initiator with diphenyl phosphate as a catalyst in dichloromethane at room temperature. The ^{1}H NMR, gel permeation chromatography (GPC), and MALDI-TOF-MS measurements of the resulting poly(δ-valerolactone)s clearly indicate the presence of the rotaxane structure with the polymer chain, confirming that the diphenyl phosphate-catalyzed ROP of VL proceeds without deslippage of the wheel component. The obtained macromolecular [2]rotaxane was acetylated to afford a nonionic macromolecular [2]rotaxane, in which only one wheel component is movable from one end to another along the polymer chain.



Polymer rotaxanes are attracting considerable attention owing to their wide range of utility derived from the structural characteristics of their topological bonding and the dynamic nature of the components. The synthesis and application of polymer rotaxanes, mainly of main-chain-type polyrotaxanes,[1−7] have been extensively studied for many years. Among structure-definite polyrotaxanes, macromolecular [2]-rotaxane, a simplest example of a polymer rotaxane, consisting of one polymer chain and one ring, has great potential in molecular machines[8−11] and block copolymer technologies[12−14] because of its controllable location, mobility, and deslippage of the components. Although many reports on polymer rotaxanes have been presented in the last two decades,[15−26] there is only one report[27] on macromolecular [2]rotaxanes by Fustin et al., who prepared it by a metal template method. There are no macromolecular [2]rotaxanes possessing crown ether or cyclodextrin wheels, despite them being the most popular wheel components of rotaxanes, most probably owing to the difficulty in synthesizing them. As previously mentioned, macromolecular [2]rotaxanes are sought after because of their wide ranging potential uses; therefore, we have investigated new synthetic strategies. Recently, we have discovered a high-yield synthetic procedure for macromolecular [2]rotaxanes with a crown ether wheel that can be utilized in various sophisticated systems. In this paper, we describe macromolecular [2]rotaxanes having controlled location of the components, which are prepared by a "rotaxane-from method".

The synthetic strategy of the macromolecular [2]rotaxane via the rotaxane-from method is depicted in Scheme 1. To ensure the introduction of one wheel component on a polymer chain,

Scheme 1. Synthetic Strategy of Macromolecular [2]Rotaxane



stable pseudo[2]rotaxane, which can maintain its structure by the strong attractive interaction between the components, was chosen as the key compound from which the axle end can initiate polymerization. A pseudo[2]rotaxane initiator consists of a *sec*-ammonium axle and a dibenzo-24-crown-8-ether (DB24C8) wheel[28−39] and extends its axle via living polymerization to give a macromolecular [2]rotaxane through the end-capping reaction of the living end with a bulky stopper.

The most important point in the synthesis of the macromolecular [2]rotaxane is to preserve the pseudo[2]-rotaxane structure during the initiation, propagation, and end-capping processes. To prevent deslippage of the DB24C8 wheel from the axle component of the pseudo[2]rotaxane initiator

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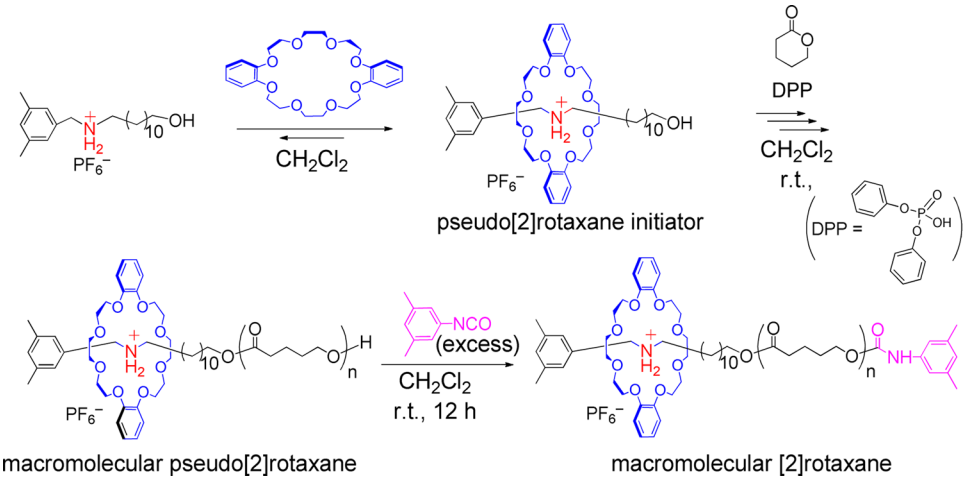
Scheme 2. Synthesis of Macromolecular [2]Rotaxane



during the series of the reactions,[40−42] we used the excellent living polymerization system reported by Kakuchi et al.[43] The living polymerization yielding poly(*δ*-valerolactone) (PVL) and poly(*ε*-caprolactone) (PCL) is performed by the selective ring-opening polymerization (ROP) of *δ*-valerolactone (VL) and *ε*-caprolactone (CL) and initiated by an alcoholic compound in the presence of diphenyl phosphate (DPP) as an organocatalyst, as per Kakuchi et al.'s method.[43] Since polymerization proceeds under weak acidic conditions, the pseudo[2]rotaxane initiator having a hydroxy axle terminal undergoes the ROP of VL without any decomposition to afford a macromolecular [2]rotaxane via the end-capping reaction with a bulky isocyanate in a high efficiency. The detailed pathways for synthesizing macromolecular [2]rotaxanes via the rotaxane-from method are shown in Scheme 2.

To a solution of a pseudo[2]rotaxane initiator synthesized in situ by the complexation of a *sec*-ammonium salt with both bulky and OH termini and DB24C8 in dichloromethane were added VL and DPP (10 mol %) at ambient temperature. Polymerization was initially carried out with a $[VL]_0/[initiator]_0/[DPP]_0$ ratio of 25/1/1. The polymerization proceeded homogeneously and was quenched after 2 h by the addition of an end-capping reagent 3,5-dimethylphenyl isocyanate to the hydroxyl terminal at the propagation end. The resulting polymer was purified by reprecipitation and then underwent preparative gel permeation chromatography (GPC) to remove excess DB24C8. The isolated yield of the macromolecular [2]rotaxane consisting of PVL as the axle polymer (PVL25-Ro) was 88%. To our surprise, the macromolecular pseudo[2]rotaxane formed before the end-capping reaction could be isolated by the direct precipitation of the polymerization mixture into an ethanol/hexane 1/9 (v/v) mixed solvent. The results indicate excellent stability of the product, without deslippage of the wheel component during isolation.

The chemical structure of PVL25-Ro was determined by ^{1}H NMR and MALDI-TOF-MS. In the ^{1}H NMR spectrum shown in Figure 1, the multiplet signal around 4.5 ppm (signal d), which is common in all three spectra (a)−(c), is a characteristic of the benzylic proton signal of the *sec*-ammonium moiety encapsulated by DB24C8 through hydrogen bonding. The phenyl proton of the *ω*-chain end appeared at 7.1 and 6.7 ppm, as shown in Figure 1(c). In addition to these, characteristic peaks of the PVL moiety (signals A, B, and C) as well as the

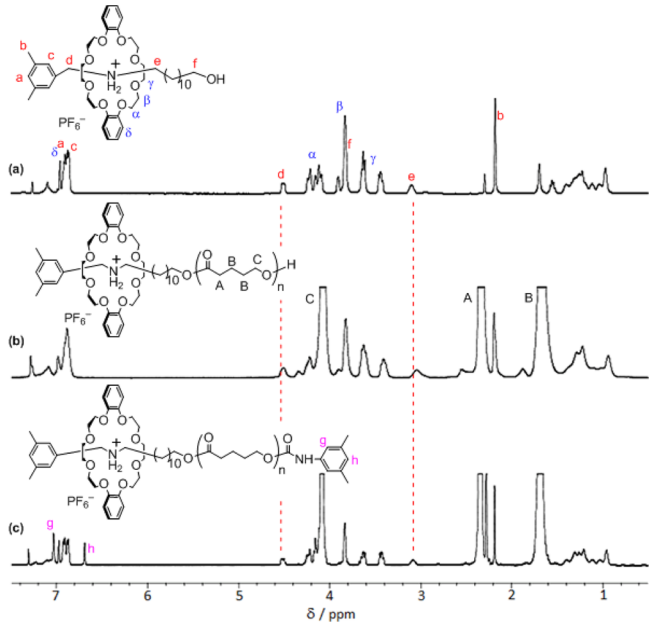


Figure 1. ^{1}H NMR spectra of the (a) pseudo[2]rotaxane initiator, (b) macromolecular pseudo[2]rotaxane PVL−OH, and (c) macromolecular [2]rotaxane, PVL25-Ro (400 MHz, $CDCl_3$, and 298 K).

specific peaks for *α*, *β*, and *γ* protons of the DB24C8 moiety around 3.3−4.3 ppm clearly indicate the formation of the macromolecular [2]rotaxane PVL25-Ro (Figure 1(c)) from the polymerization of VL initiated by the pseudo[2]rotaxane initiator followed by the end-capping reaction with 3,5-dimethylphenyl isocyanate. MALDI-TOF-MS (Figure S13, Supporting Information) results also indicate that the *sec*-ammonium/crown ether-type complex was stable during the ROP of VL.

MALDI-TOF-MS of PVL25-Ro provides direct evidence that the ROP of VL, initiated from the pseudo[2]rotaxane initiator, proceeds while maintaining the rotaxane structure. Figure 2 shows the MALDI-TOF-MS spectrum of PVL25-Ro, demonstrating that a series of peaks perfectly correspond to the molecular weight of PVL possessing both the pseudo[2]-rotaxane initiator group and the 3,5-dimethylphenylurea group as the chain end. This result strongly indicates that the DPP-catalyzed rotaxane-from polymerization and the subsequent

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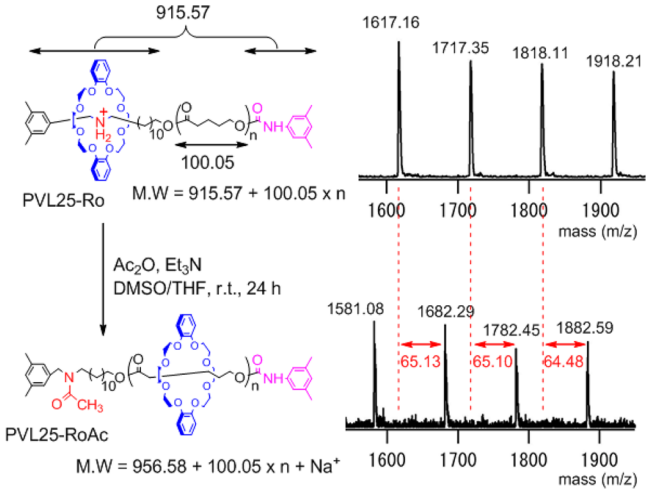

Figure 2. MALDI-TOF-MS of PVL25-Ro and RVL25-RoAc (linear mode).

end-capping reaction successfully proceed in high yield without deslippage of the wheel component.

Similar ROPs of VL in different feed ratios were conducted to synthesize longer axle polymers. Table 1 summarizes the polymerization conditions and results. The feed ratio of monomer to initiator ($[M]_0/[I]_0$) changes from 25 to 100, while the feed ratio of DPP was fixed. The molecular weights of the resultant PVLs linearly increased with an increase in the feed ratio of $[M]_0/[I]_0$, whereas their polydispersity indices were relatively narrow in each case. Unimodal GPC profiles for the PVL-Ro's are also observed (Figure S3, Supporting Information).

To confirm the versatility of this method, additional polymerizations using different monomers and initiators were carried out. As Kakuchi et al. reported a DPP-catalyzed ROP system available for CL as well as VL, we synthesized a macromolecular [2]rotaxane with a PCL axle by a similar method (Table 1, Scheme S3, Supporting Information). The ^{1}H NMR and MALDI-TOF-MS data (Figures S4 and S5, Supporting Information) of the resulting polymer indicate that the synthesis of the DPP-catalyzed ROP of CL is successful, without deslippage of the wheel component, even though the polymerization rate of CL is much slower than that of VL. In addition, a different type of pseudo[2]rotaxane initiator having a dibenzyl ammonium/DB24C8 complex as the pseudo[2]-rotaxane was synthesized as an initiator for VL (Scheme S2, Supporting Information). This pseudo[2]rotaxane is known to be sufficiently stable,[44] and this macromolecular [2]rotaxane was also obtained without any deslippage of DB24C8 (Table 1, Scheme S4 and Figures S7 and S8, Supporting Information).

The results of the kinetic analysis of the ROP of VL using the pseudo[2]rotaxane initiator (Figure S9(a), Supporting Information) revealed that the polymerization proceeded in a living fashion. In addition, the rate of the polymerization with the pseudo[2]rotaxane initiator was almost the same as that with a model initiator, 3-phenyl 1-propanol (Figure S9(a), Supporting Information). Therefore, the pseudo[2]rotaxane structure does not affect the DPP-catalyzed polymerization, in spite of the presence of the ammonium PF_6^- ionic complex residue. The linear correlation between molecular weight and the conversion (Figure S9(b), Supporting Information) also suggested the living nature with high initiator efficiency compared to the theoretical value. Consequently, the facile synthesis of pure macromolecular [2]rotaxanes in high yields could be established via the rotaxane-from method in this study.

Although a macromolecular [2]rotaxane was first synthesized by Fustin et al.,[27] the most intriguing property of macromolecular [2]rotaxanes is the dynamic nature of the components, i.e., the translation of the wheel component along the axle polymer chain.

Thus, the ammonium salt moiety was neutralized to remove the hydrogen bonds between the ammonium protons and DB24C8 that made translation impossible. We have already reported the neutralization of ammonium/crown ether-type rotaxanes by several methods.[45−50] One of the most effective methods is selective N-acylation with an electrophile in the presence of a base. This method was applied to a macromolecular [2]rotaxane using acetic anhydride and triethylamine. Figure 2 shows the MALDI-TOF-MS spectrum of the acetylated polymer, PVL25-RoAc. A series of peaks perfectly corresponded to the molecular weight of the N-acetylated macromolecular [2]rotaxane PVL25-RoAc. Compared to the molecular mass of PVL25-Ro, an increase by ca. 65 Da is consistent with the molecular weight of an acetyl group and a sodium cation added during the measurement. Figure S10 (Supporting Information) shows the ^{1}H NMR spectra of PVL25-RoAc. The *N*-benzyl proton signal around 4.5 ppm changed from a broad peak (Figure 1) to a couple of sharp signals, clearly indicating the occurrence of N-acetylation.

Acetylative neutralization of PVL25-RoAc seems to cause the free movement of the wheel component, DB24C8, along the axle polymer chain because attractive interaction between the axle polymer and DB24C8 is diminished. It is very interesting to find the position on the axle where the wheel component is localized mostly. From the ^{1}H NMR data, the wheel component might be moving along the polymer chain, but there is no evidence that the wheel component really travels through the whole axle polymer chain. To confirm the mobility of the wheel component, we carried out the neutralization of the macromolecular pseudo[2]rotaxane (Scheme S6, Support-

Table 1. DPP-Catalyzed ROP of Lactone Monomers from Pseudo[2]rotaxane Initiators[a]

code	monomer	$[M]_0/[I]_0$	yield[b] (%)	DP_n[c]	M_n[d]	M_w/M_n[d]
PVL25-Ro	VL	25	88	22.8	4200	1.5
PVL50-Ro	VL	50	91	44.8	7000	1.2
PVL100-Ro	VL	100	90	92.7	11300	1.2
PCL25-Ro	CL	25	93	23.0	5000	1.4
PCL25-DBRo[e]	VL	25	80	21.1	4400	1.1

[a]Polymerization condition: $[I]_0$ = 40 mmol/L, $[DPP]_0/[I]_0$ = 1, and rt. [b]Isolated yield after preparative GPC eluted with $CHCl_3$. [c]Degree of polymerization determined by ^{1}H NMR. [d]Determined by GPC eluted with THF on the basis of polystyrene standards. [e]Dibenzyl ammonium-type pseudo[2]rotaxane initiator was used.

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ing Information), which was isolated by reprecipitation before the end-capping reaction. After the acetylation of the macromolecular pseudo[2]rotaxane, the reaction mixture was directly subjected to preparative GPC shown in Figure 3(a).

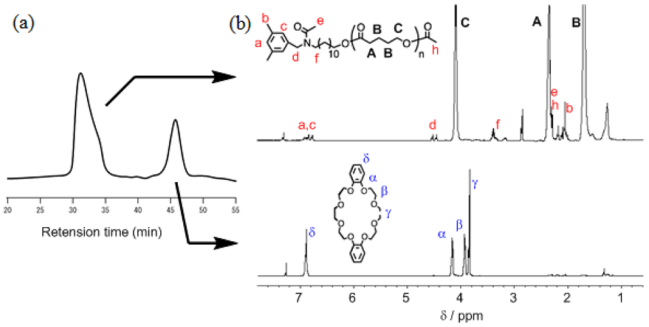

Figure 3. ^{1}H NMR spectra of each fraction separated by the preparative GPC of acetylated macromolecular pseudo[2]rotaxane (400 MHz, $CDCl_3$, and 298 K).

Two major peaks were observed in the GPC trace, and each peak was separated and characterized by ^{1}H NMR and MALDI-TOF-MS (Figure S15, Supporting Information). Figure 3(b) shows the ^{1}H NMR spectra of the two products, indicating that the earlier fraction is the axle polymer while the latter one is DB24C8. Since there are only two peaks in the GPC profile, the macromolecular pseudo[2]rotaxane has perfectly dissociated into the corresponding axle polymer and DB24C8. This result undoubtedly proves that DB24C8 can move from one end to the other along the PVL chain. Considering this result, the wheel component of the acetylated macromolecular [2]rotaxane can also travel along the whole axle polymer chain.

In conclusion, we have achieved an effective synthetic method for a macromolecular [2]rotaxane by the rotaxane-from strategy. It is achieved through the DPP-catalyzed ROP of VL and CL using a *sec*-ammonium-type pseudo[2]rotaxane initiator having a hydroxyl group at the axle terminal, followed by an end-capping reaction at the propagation end. The pseudo[2]rotaxane structure did not affect polymerization, which proceeds in a living fashion, although its *sec*-ammonium moiety remained. The removal of the attractive interaction between the ammonium moiety and DB24C8 of a macromolecular [2]rotaxane by acetylation allowed the free movement of the wheel component along the whole axle polymer chain. This was the first example of a macromolecular [2]rotaxane in which the wheel component can travel along the whole axle polymer chain. Since the present effective synthetic method should make large-scale synthesis possible, it may allow for the development of novel materials having dynamic properties, which are changeable, according to the mobility of the components.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, ^{1}H NMR, FTIR, MALDI-TOF-MS, and GPC data used for the present study are given. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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