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Mechanically Linked Block/Graft Copolymers: Effective Synthesis via Functional Macromolecular [2]Rotaxanes

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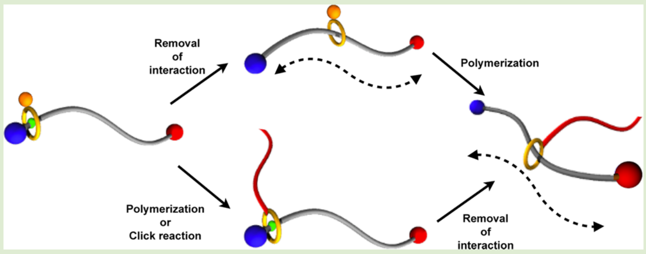
Supporting Information

ABSTRACT: An effective method to synthesize mechanically linked transformable block polymer was developed utilizing functional macromolecular [2]rotaxane with a “fixed” or “movable” wheel. The interaction between a *sec*-ammonium and a dibenzo-24-crown-8-ether was the key to control the mobility of the wheel component, indicating the capability of the transformation from linear block copolymer to block/graft copolymer in which the grafting polymer chain is movable along the axle polymer chain.



Over the last few decades, the evolution of controlled or living polymerization techniques[1−8] and efficient coupling reactions, commonly known as click chemistry,[9−14] have opened up the field of polymer science to achieve a great variety of well-defined geometric macromolecular architectures. Block copolymers with intricate backbones such as star-shaped,[15,16] comb-shaped, or cyclic structures[17,18] are contemplated to form higher-ordered self-assembled structures either in bulk or in the presence of selective solvents. Further, it is envisaged that the integration of functional moieties on the polymer segments could lead to their use for miscellaneous applications. Differences in the backbone structures of block copolymers have recently been recognized as an important factor for facilitating the formation of self-assembled structures[19−21] and are also well-known to affect the physical properties of the block copolymer materials. Therefore, transformable block copolymers, which can transfigure the topology of their polymer backbones, are of great potential for the development of polymer materials with desirable properties such as stimuli responsibility, self-mending aptitude, and shape-memory effects. The key of this work was incorporation of a rotaxane structure[22−34] into a block copolymer as a junction point. Fustin et al. have reported[35] on the synthesis of a rotaxane-linked block copolymer, containing poly(methyl acrylate) (PMA) and poly(ethylene oxide) (PEO) connected to a rotaxane structure, which they named PMA-*rot*-PEO. The qualifier “*-rot-*” was ingeniously spelled out to emphasize the difference against the other copolymers,[36−41] indicating the high potential of transformable block copolymers. The polymer made of covalent bond seem to be unsuitable for the transformable block copolymer because of hard constitution, which stimulated us to focus on the rotaxane structure in which mechanically linked wheel component can move freely through the axle. Recently, we have established an efficient synthetic method for the formation of macromolecular [2]rotaxanes with a high yield, consisting of a polymer chain threaded into a wheel molecule, by means of the polymerization of lactone monomers from a pseudo[2]rotaxane initiator.[42] In addition, we have demonstrated the slippage of the wheel molecule from the polymer chain in the absence of a bulky end-capping group on the ω-end of the macromolecular [2]rotaxane.

In this paper, we report on the application of this efficient method for the synthesis of movable mechanically linked block/graft copolymers via both the grafting-onto and grafting-from pathways, using wheel molecules with various functional groups.

The synthetic strategy for the formation of mechanically linked block/graft copolymers via a functional macromolecular [2]rotaxane is depicted in Scheme 1.

To ensure the introduction of a single-wheel component onto a polymer chain, a stable pseudo[2]rotaxane that can maintain its structure through strong attractive interactions between the components,[43−59] was chosen as the key compound from which the end-functionalized group of the axle molecule can initiate the polymerization reaction. A pseudo[2]rotaxane initiator consists of a *sec*-ammonium axle and a functional dibenzo-24-crown-8-ether (DB24C8) wheel, as shown in Scheme 2.

Its axle is extended via a diphenylphosphate (DPP)-catalyzed living ring-opening polymerization (ROP) of δ-valerolactone (VL) and terminated with the capping of the living end with a bulky stopper, so as to give a secure macromolecular [2]rotaxane with a functional group on the wheel component. The resulting functional macromolecular [2]rotaxanes were utilized to synthesize rotaxane-linked block copolymers.

As shown in Scheme 2, a wide variety of functional groups were selected for the synthesis of mechanically linked block

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Scheme 1. Synthetic Strategy for the Functional Macromolecular [2]Rotaxane and Mechanically Linked Block/Graft Copolymers

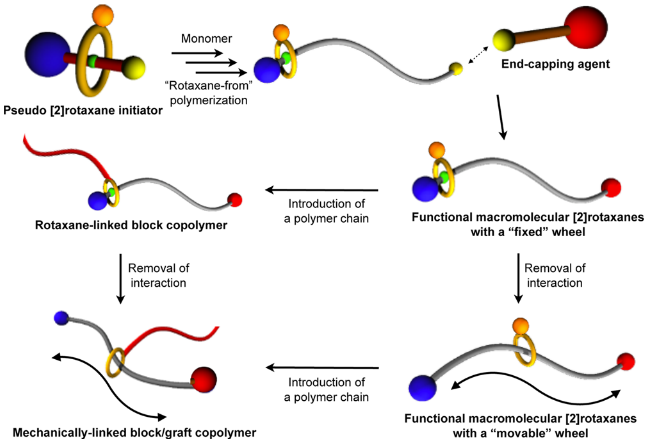


Table 1. DPP-Catalyzed ROP of δ-Valerolactone from Various Functional Pseudo[2]rotaxane Initiators[a]

code	yield[b] (%)	$M_{n,NMR}$[c]	$M_{n,GPC}$[d]	M_w/M_n[d]
PVL-BiB_F	75	6400	3400	1.3
PVL-TTC_F	89	6800	3300	1.3
PVL-Alkene_F	77	6500	3800	1.3
PVL-Alkyne_F	73	6800	3300	1.4
PVL-Azide_F	83	6500	3200	1.3
PVL-Anth_F	83	6300	3900	1.3
PVL-Aldehyde_F	89	7000	3000	1.4
PVL-TIPS_F	70	6800	3300	1.3
PVL-MA_F	71	6900	3400	1.3

[a] Polymerization condition: $[I]_0$ = 40 mmol/L, $[DPP]/[I]_0$ = 1, $[M]_0/[I]_0$ = 50 in dichloromethane at room temperature (rt) for 2 h. [b] Isolated yield after preparative GPC eluted with chloroform. [c] Determined by ^{1}H NMR in $CDCl_3$ at rt. [d] Determined by GPC eluted with tetrahydrofuran (THF) on the basis of polystyrene standards.

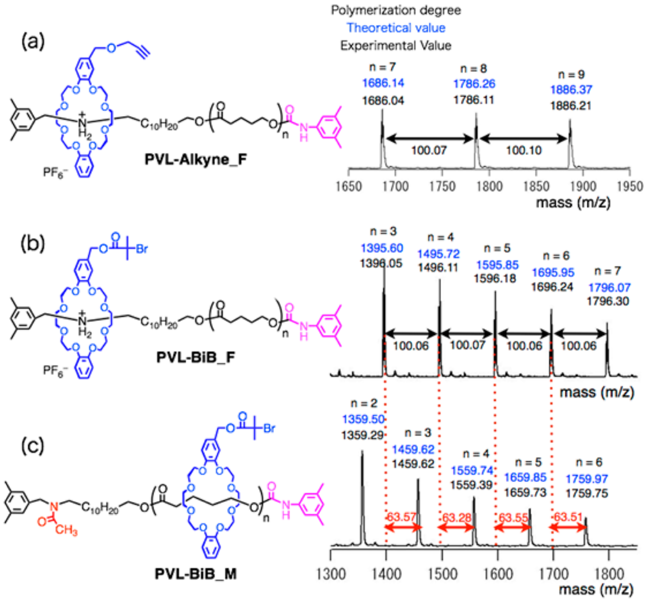


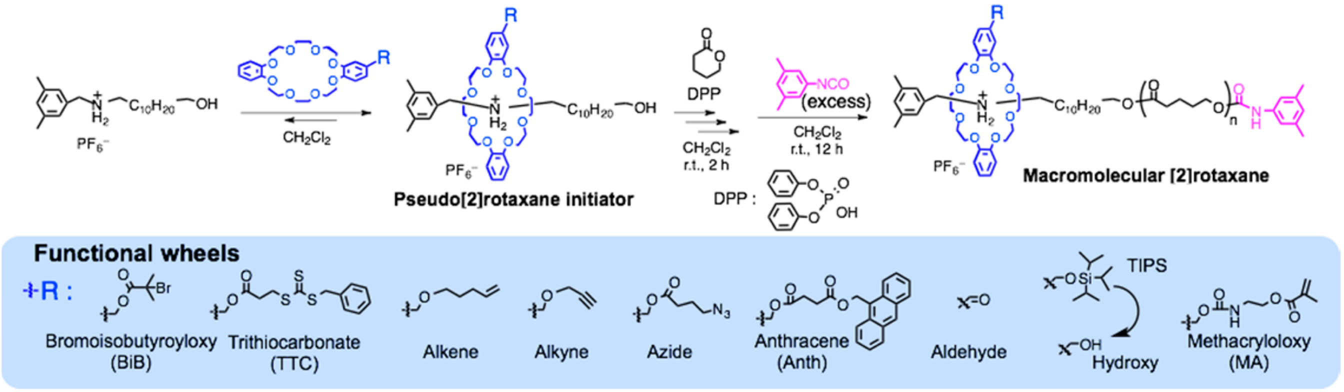
Figure 1. MALDI-TOF-MS spectra of typical functional macromolecular [2]rotaxanes.

copolymers via either grafting-onto or grafting-from pathways, preparing the macroinitiators for the further polymerization or the functional precursors for a click reaction. Table 1 summarizes polymerization results of aforementioned functional macromolecular [2]rotaxanes.

Relatively high isolated yields (70−89%) for all of the resulting polymers were observed, indicating that these functional groups were not affected by the DPP-catalyzed ROP of VL. The molecular weight of poly(δ-valerolactone)s (PVLs), initiated from various functional pseudo[2]rotaxane initiators, calculated from ^{1}H NMR spectra corresponded to the feed monomer ratio and gave a relatively narrow polydispersity index in each case. The molecular weight determined by GPC was underestimated due to the smaller hydrodynamic volume than that of polystyrene. ^{1}H NMR[60] and MALDI-TOF-MS spectra of the resultant polymers provide direct evidence of the synthesis of functional macromolecular [2]rotaxanes. Figure 1a,b show the MALDI-TOF-MS spectra of functional macromolecular [2]rotaxanes with alkyne and BiB groups.

A series of peaks with an interval of 100.05 Da can be seen that correspond to the molecular weights of PVL, possessing both the pseudo[2]rotaxane initiating group and 3,5-dimethylphenylurea as the end-capping group. These results are consistent with the DPP-catalyzed ROP and the subsequent end-capping reaction proceeding successfully to afford the functional macromolecular [2]rotaxane with high isolated yield, indicating no occurrence of side reactions on the functional groups or deslippage of the functional DB24C8 during the polymerization. The most intriguing property of macro-

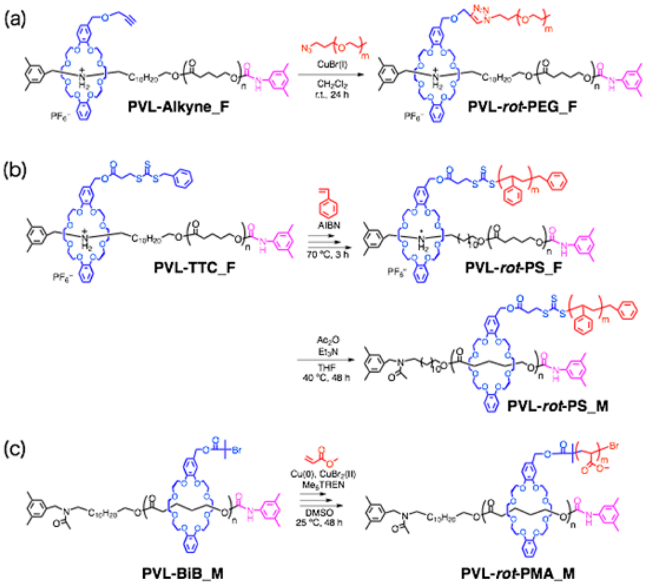
Scheme 2. Synthesis of the Functional Macromolecular [2]Rotaxanes



molecular [2]rotaxanes is the dynamic nature of their components, that is, the ability for wheel component to move along the axle polymer chain. The ammonium moiety was neutralized to remove the hydrogen bonds between the ammonium protons and the DB24C8 oxygens enabling the free movement of the wheel. We have previously reported[61−65] the neutralization of ammonium/crown ether-type rotaxanes by *N*-acylation with an electrophile in the presence of a base. This reaction was applied to functional macromolecular [2]rotaxanes bearing an initiator moiety for ATRP, PVL-BiB_F (suffix F indicates a "fixed" wheel component), using acetic anhydride and triethylamine as an electrophile and a base, respectively. Figure 1c shows the MALDI-TOF-MS spectrum of the acetylated macromolecular [2]rotaxane PVL-BiB_M (suffix M indicates a "movable" wheel). A series of peaks can be seen that perfectly correspond to the molecular weight of the *N*-acetylated macromolecular [2]rotaxane PVL-BiB_M. Compared to the molecular mass of PVL-BiB_F, the observed increase of about 64 Da is consistent with the molecular weight of an acetyl group and a sodium cation added for the MALDI-TOF-MS measurement. The mobility of the crown ether of the acetylated macromolecular [2]rotaxane has been previously reported.[42] It is described that the crown ether was delocalized along the polymer axle chain and deslippage of the crown ether was observed in macromolecular pseudo[2]rotaxanes, which had no bulky end-capping groups.

To synthesize rotaxane-linked block copolymers, PVL-Alkyne_F, PVL-TTC_F, and PVL-BiB_M were adopted for both grafting-onto and grafting-from pathways, with a polymer chain tethered to the wheel component. First, PVL-Alkyne_F was subjected to a copper catalyzed alkyne−azide click reaction with an azide end group on PEG as shown in Scheme 3a. After the reaction, the rotaxane-linked block copolymer PVL-*rot*-PEG_F was isolated by fractionation technique and preparative GPC. The ^{1}H NMR spectrum[60] of the resultant copolymer showed the expected peaks as derived from both PVL and PEG segments with no alkyne peak. In addition, the unimodal peak of GPC profile[60] confirmed the synthesis of rotaxane-linked copolymer PVL-*rot*-PEG_F.

Scheme 3. Synthesis of Rotaxane-Linked Copolymers



The grafting-from pathway was also employed to synthesize rotaxane-linked copolymers using functional macromolecular [2]rotaxanes as a macroinitiator, as shown in Scheme 3b. PVL-TTC_F was subjected to RAFT polymerization of styrene using AIBN as a radical source was carried out at 70 °C for 4 h. The obtained polymer was purified by reprecipitation and preparative GPC.

The GPC profile[60] of the resultant polymer displayed a unimodal peak, and ^{1}H NMR spectra shown in Figure 2a,b indicate the synthesis of PVL-*rot*-PS_F, as determined from the appearance of the huge peaks consistent with the presence of a benzene ring (E) and the disappearance of the benzyl trithiocarbonate peak (X). As for the rotaxane structure, no change of the chemical shifts corresponding to the crown ether (α, β, γ) before and after RAFT polymerization, indicated that the *sec*-ammonium/crown ether-type complex was stable during the RAFT polymerization. Therefore, the wheel component attached with a dangling polystyrene chain encapsulated the *sec*-ammonium moiety, meaning the whole polymer topology was linear block copolymer.

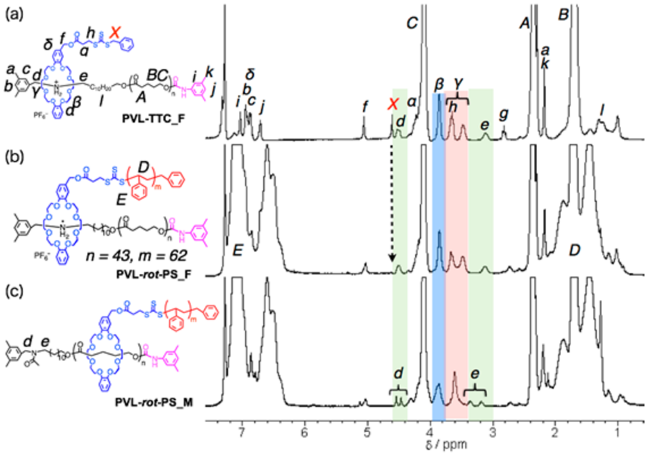


Figure 2. ^{1}H NMR spectra of (a) PVL-TTC_F, (b) PVL-*rot*-PS_F, and (c) PVL-*rot*-PS_M in $CDCl_3$ (400 MHz, 298 K).

The ammonium moiety was then neutralized (as described previously) to release the DB24C8 ring with a dangling polystyrene chain forming a mechanically linked block/graft copolymer. The ^{1}H NMR spectrum of the obtained copolymer (Figure 2c) showed the characteristic split peaks of the methylene protons adjunct to the acetylated nitrogen (d and e), indicating successful acetylation of ammonium moiety. In addition, the methylene protons of DB24C8 (γ) turned from split peaks to a single peak, implying the removal of the interaction with the ammonium moiety. No decomposition reaction or condensation reaction was observed in the GPC profile[60] of the obtained copolymer and the synthesis of a mechanically linked block/graft copolymer, PVL-*rot*-PS_M, was confirmed. As it is very interesting to elucidate where the wheel component is localized on the axle, ^{1}H NMR data did not indicate the specific correlation with the axle component to conclude the delocalization of the wheel component.

Scheme 3c shows another synthetic pathway of the synthesis of a mechanically linked block/graft copolymer via a grafting-from strategy. PVL-*rot*-PMA_M was synthesized via single electron transfer ATRP of methyl acrylate initiated from PVL-BiB_M, which has a movable initiating group. ^{1}H NMR spectra and GPC profiles[60] of the obtained copolymer showed the synthesis of PVL-*rot*-PMA_M was successful. In this method, the acetylation has been done prior to the attachment of the graft polymer chain, indicating that this method is useful to the polymers sensitive to the acetylation, such as hydroxyl and amine-bearing polymers. We achieved the synthesis of mechanically linked block/graft copolymers through functional macromolecular [2]rotaxane with a fixed and moveable wheel.

In conclusion, we developed an effective synthetic method for the mechanically linked block/graft copolymers utilizing functional macromolecular [2]rotaxanes by the applying "rotaxane-from" strategy. The use of various pseudo[2]rotaxane initiators, employing a number of functional groups on the wheel molecule, did not affect the DPP-catalyzed ring-opening polymerization of δ-valerolactone. Mechanically linked block/graft copolymers were synthesized by the introduction of another polymer chain onto the wheel molecules via grafting-onto and grafting-from pathways. This was the first example of a transformable block/graft copolymer in which the grafting polymer chain is able to travel along the whole axle polymer chain. Although the further research on the mobility of the graft chain is under way, this work paves the way for the formation of novel block copolymers with dynamic transformations owing to topological changes in their polymer backbones. These properties are expected to lead to unique concepts of the rotaxane-linked polymers for various materials such as high-impact, shape memory, and self-mending materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional experimental details. 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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