Supramolecular Transformation of Metallacycle-linked Star Polymers Driven by Simple Phosphine Ligand-Exchange Reaction

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Supporting Information

ABSTRACT: As a common phenomenon in biological systems, supramolecular transformations of biomacromolecules lead to specific biological functions as outputs, which thus inspire people to construct biomimetic dynamic systems through supramolecular transformation strategy. It should be noted that well-modulating the artificial macromolecules to fine-tune their properties is of great significance yet still remains a big challenge in polymer chemistry. In this study, through the combination of coordination-driven self-assembly and postassembly ring-opening polymerization, a six-armed star polymer linked by well-defined hexagonal metallacycle as core was successfully prepared. At the same time, the trans-platinum acetylde moieties as transformation sites were anchored onto the discrete metallacycle scaffold. Subsequently, the simple phosphine ligand-exchange reaction induced the conversions of platinum acetylide building blocks with the varied binding angles, which thus resulted in the successive hexagon–rhomboid–hexagon transformations of metallacyclic scaffold, therefore allowing for the corresponding supramolecular transformation of metallacycle-linked star polymers. More importantly, accompanied by such transformation process, property modulation of the resultant polymers has been successfully realized. In a word, by taking advantage of dynamic nature of metal–ligand coordination bonds and simple phosphine ligand-exchange reactions, facile architecture transformation of a star polymer to a linear polymer and back to a star polymer was successfully realized, which may provide a promising approach toward the construction of new dynamic polymeric materials.

INTRODUCTION

It is well-known that stimuli-induced structural changes of biomacromolecules such as proteins, DNA, RNA, etc., are capable of achieving specific biological functions, which plays an important role in many life processes in biological systems. An enhanced understanding of such biological transformation processes with the output of specific functions will be beneficial to not only the comprehension of basic biological principles but also the construction of biomimetic functional materials. Thus, at the molecular level, synthetic chemists have been working on design and synthesis of a great number of molecular systems with a transformable scaffold during past decades. Recently, architecture-transformable polymers have evolved to be one of the most attractive topics within polymer chemistry and materials science because of their prospective applications in biological and artificial self-adaptive materials. In general, architecture-transformable polymers are very “smart” to change their topological structures when being triggered by a specific external stimulus. In particular, along with such architectural transformation, the physical and morphological properties of polymers such as hydrodynamic volume, viscosity, and crystallinity can be rationally regulated, thus allowing for the construction of new dynamic functional materials. Therefore, a great deal of efforts on the design and construction of architecture-transformable polymers have been witnessed during the last two decades. For instance, by taking advantage of the unique reversible-covalent chemistry,

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Sumerlin and co-workers demonstrated the structural interconversions between polymers with diverse architectures guided by the concept of macromolecular metamorphosis. Johnson and co-workers reported the photocleavable brush-arm star polymers (BASPs) that can be selectively UV-degraded to form star polymers. As above-mentioned, supramolecular transformation strategy has been widely employed to fine-tune the structures and functionality of biological scaffolds in nature. By taking advantage of dynamic nature of noncovalent interactions, recent investigations have demonstrated that supramolecular transformation strategy allows for in situ structural interconversions between polymers with varied topological structures. For example, through the introduction of mechanical linking such as rotaxane or [c2] daisy chain units into the polymer skeleton, a series of architecture-transformable polymers have been realized by Takata and co-workers. Thus, supramolecular transformation methodology provides an alternative way to readily produce a wide variety of polymers with different structures and properties. Among diverse artificial supramolecular transformation systems, the ones based on metallosupramolecular assemblies have attracted more and more attention due to the high efficiency, mild conditions, and diverse topological structures. However, the architecture transformation of polymers based on discrete metallacycles or metallacages has been rarely reported. The only example was recently demonstrated by Johnson and co-workers, in which the architecture transformation of polymer gel cross-linked by metal–organic cages was successfully realized by photoswitching. Considering the diversity of structures and functionalities of metallosupramolecular architectures, the construction of architecture-transformable polymers linked by metallacycles or metallacages will provide an opportunity to prepare new dynamic functional materials.

Scheme 1. Schematic Representation of the Configure Transitions of Platinum Acetylide Moiety through Simple Phosphine Ligand-Exchange Reaction

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**RESULTS AND DISCUSSION**

**Construction of Star Polymer Linked by Hexagonal Metallacycle via Postassembly Polymerization.** In this study, postassembly polymerization strategy, which has proven to be a highly efficient methodology to introduce polymeric chains into the discrete metallosupramolecular structures with the fine-tuning structures and desired properties, was employed to build six-armed star polymer possessing a well-defined hexagonal metallacycle as the main scaffold. According to the general principles of coordination-driven self-assembly, the construction of hexagonal metallacycle could be realized through combination of six 120° precursors with six 180° building blocks. Thus, 120° di-Pt(II) acceptor subunit containing hydroxy group for the subsequent controlled ring-opening polymerization and the linear donor building block with trans-platinum acetylide moiety as the transformation site were designed and synthesized, respectively. The hexagonal metallacycle containing six primary hydroxy groups at alternative vertices as the initiating sites was prepared in 96% yield by simply stirring the mixture of di-Pt(II) acceptor 3 containing hydroxy group for the subsequent controlled ring-opening polymerization and the linear donor 4 in a 1:1 ratio in aceton-d₆ at room temperature for 8.0 h (Scheme 2). The structure of hexagonal metallacycle 5 was well characterized by means of multinuclear NMR (¹H and ³¹P) spectroscopy (Figure S1) and ESI-TOF-MS spectrometry (Figure 1a).

Subsequently, the desired metallacycle-linked star polymer 8 was prepared by polymerizing ε-caprolactone in the presence of the corresponding diphenyl phosphate (DPP) as a catalyst as well as an initiator with a molar ratio of [ε-caprolactone]/[DPP]/[initiator] = 600:2:1 in dichloromethane at room temperature for 8.0 h in a glovebox. The resulting mixture was purified by reprecipitation in cold n-hexane to afford the star polymer 8. In-depth analysis of multinuclear (¹H and ³¹P) NMR spectroscopy, FTIR, and gel permeation chromatography (GPC) provided the strong evidence for the formation of the desired star polymer 8. For example, in the ¹H NMR spectrum, the characteristic signals of poly(ε-caprolactone) (PCL), including δ = 4.05, 2.31, 1.62, 1.40 ppm attributed to the methylene protons of caprolactone groups, respectively, were observed in the ¹H NMR spectrum (Figures 2a and S7). It should be noted that, compared to the metallacycle 5, the ³¹P {¹H} NMR spectrum of polymer 8 displayed two singlets at 20.13 and 14.46 ppm, which remained almost unchanged (Figure 2b). This observation demonstrated that the controlled postassembly polymerization allowed for the formation of six-armed star polymers with the well-defined hexagonal metallacycle as the core in this study. Gel permeation chromatography (GPC) analyses gave a number-average molecular weight (Mₙ) of 60.0 kDa and a polydispersity index (PDI) of 1.30 for 8 (Figure 3a). In addition, the degree of polymerization (DP) of PCL in each arm was determined to be 40 through ¹H NMR characterization. According to the results of the PM6 semiempirical molecular orbital simulation, metallacycle 5 featured a hexagonal ring at their core with the internal diameters of 5.1 nm (Figure S4). Thus, the star-shaped polymer 8 featured a relatively rigid metallacycle as the core and six flexible arms.
Supramolecular Transformation of Model Hexagonal Metallacycles. With the targeted transformable polymer 8 in hand, its precursor, the hexagonal metallacycle 5, was first employed as a model system to investigate the feasibility of multistep supramolecular transformations driven by phosphine ligand-exchange reaction (Scheme 3). It is worth noting that the choice of the phosphine ligands was based on their different chelating ability and electron-donating ability toward the central platinum atom. Thus, chelating diphosphine ligands cis-1,2-bis(diphenylphosphino)ethylenes (DPPEE) and monophosphine ligand triethylphosphine (PEt₃) were chosen to replace the PPh₃ ligand to realize the transformation processes. Upon adding different equivalents of DPPEE into the acetone-<i>d₆</i> solution of hexagon 5, both multiple nuclear NMR (Figure S3) and ESI-TOF-MS (Figure 1) results indicated the formation of new discrete metallostructures by simply adding new phosphine ligand. During this supramolecular transformation process, the only byproduct was the replaced PPh₃ ligand, which can be easily removed through the continuous wash of the obtained product with <i>n</i>-hexane. After this easily handled workup, the new metallostructure was obtained in near quantitative yield.

Figure 1. Calculated (top) and experimental (bottom) ESI-TOF-MS spectra of metallacycles 5 (a), 6 (b), and 7 (c), respectively.

Figure 2. Partial <sup>1</sup>H (a) and <sup>31</sup>P (b) NMR spectra of hexagonal metallacycle 5 and polymers 8, 9, and 10.
Upon the ligand-exchange of $\text{PPh}_3$ ligand with $\text{DPPEE}$, the trans-platinum acetylide building block converted to the cis-configured analogous with the change of the binding angle from 180° to 90°. Based on the “directional bonding” model and the “symmetry interaction” model, the combination of 90° donors and 120° di-Pt(II) acceptors prefers forming $[2 + 2]$ rhomboidal metallacycles.\textsuperscript{13} ESI mass spectrometry was then employed to identify the new species after the stoichiometric addition of $\text{DPPEE}$. The ESI-TOF-MS spectrum displayed a peak at $m/z = 1225.31$, corresponding to the charged species $[\text{M} - 3\text{OTf}]^{3+}$. In particular, this peak was isotopically resolved and is in good agreement with theoretical distribution of the $[2 + 2]$ rhomboid as shown in Figure 1b. Thus, the collected mass results along with multinuclear NMR data ensured that $[2 + 2]$ rhomboid was the product through supramolecular transformation induced by simple phosphine-ligand exchange. Consequently, all above observations clearly confirmed that the $[6 + 6]$ hexagon 5 was able to quantitatively transform into $[2 + 2]$ rhomboid 6 in response to binding angle change of donor building block 4 driven by the phosphine ligand-exchange reaction, thus providing a facile and highly efficient approach to supramolecule-to-supramolecule transformation between two different sized metallacycles. Furthermore, considering the large and diverse number of phosphine ligands with different chelating ability and electron-donating ability toward the central metal atom, the subsequent supramolecular transformation of $[2 + 2]$ rhomboid 6 was then investigated by employing the monophosphine ligand $\text{PEt}_3$ with the stronger electron-donating ability. To our delight, the transformation from $[2 + 2]$ rhomboids 6 to $[6 + 6]$ hexagon 7 was successfully realized through varying the angle between binding sites of donor building block from 90° back to 180° upon the addition of the stoichiometric amount of $\text{PEt}_3$ (Scheme 3). Both multiple nuclear NMR spectroscopy and ESI-TOF-MS results provided strong support for the success of successive supramolecular transformations (Figures S2 and 1c). All attempts to grow X-ray quality single crystals of the aforementioned metallacycles have proven to be unsuccessful to date. The molecular simulation by PM6 semiempirical molecular orbital method clearly indicated the cavity regulation of metallacycles accompanied by such multistep supramolecular transformations (Figures S4–S6).

**Supramolecular Transformation of Metallacycle-linked Star Polymers.** Based on the above results of supramolecular transformation within model hexagonal metallacycle, the subsequent investigation on multistep supramolecular transformation of metallacycle-linked polymers triggered by phosphine ligand-exchange reaction was then carried out (Scheme 4). With the addition of 0.25 equiv of $\text{DPPEE}$ into the acetone-$d_6$ solution of six-armed star polymer 8, a new phosphorus peak at $\delta = 54.85$ ppm in $^{31}\text{P}\{1\text{H}\}$ NMR spectrum was observed (Figures 2b and S12). Moreover, in the $^1\text{H}$ NMR spectrum, two new doublets attributed to the
protons on coordinated pyridine rings of new polymer at 8.70 ppm (α-H_{Py}) and 7.38 ppm (β-H_{Py}) were found (Figure 2a). Gradually increasing the amount of DPPEE from 0.25 to 1.00 equiv resulted in a diminishing of the original phosphorus peak characteristic of star polymer 8 and the simultaneous increase of the renascent peak at δ = 54.85 ppm (Figure S12). It should be noted that almost no change of the phosphine atoms on the di-Pt(II) acceptor (14.46 ppm) was observed, which indicated the existence of coordination Pt–N bonds during the addition of new phosphine ligand DPPEE (Figure 2b). Meanwhile, in 1H NMR spectrum, both α- and β-H peaks of the pyridine moieties experienced the upfield shifts of 0.23 and 0.76 ppm, respectively (Figure 2a). The change of 31P and 1H NMR spectra with the addition of DPPEE indicated the complete transformation from [6 + 6] hexagonal metallacycle-linked star polymer 8 to [2 + 2] rhomboidal metallacycle-linked linear polymer 9. Similar with the supramolecular transformation of model metallacycle 5, the successive supramolecular transformation of linear polymer 9 to a new six-armed star polymer 10 was also realized by employing the monophosphine ligand PEt3. To our delight, the multinuclear (1H and 31P) NMR spectroscopy results provided the strong support for the success of such multistep supramolecular transformations (Figure 2a,b).

Gel permeation chromatography (GPC) measurement is a general and convenient method to evaluate the molecular weight and hydrodynamic volume for polymers. Thus, GPC technique was employed to characterize the hydrodynamic volume change of the polymers before and after supramolecular transformation. As shown in Figure 3a, the narrow GPC peak of polymer 9 (M_n = 32.1 kDa, M_w/M_n = 1.23) appeared at a higher elution time than that of star polymer 8 (M_n = 60.0 kDa, M_w/M_n = 1.30). The observed shift indicated a significant decrease in hydrodynamic volume along with supramolecular transformation from a star polymer 8 to a linear polymer 9. According to the above-mentioned molecular simulation of metallacycles (the internal diameters of 5.1 nm for [6 + 6] hexagon 5 and 1.5 nm for [2 + 2] rhomboid 6), the linear polymer 9 featured a much smaller metallacycle than that of star polymer 8, which is consistent with the GPC results. Meanwhile, with the subsequent transformation of a linear polymer 9 to another star polymer 10 (M_n = 52.9 kDa, M_w/M_n = 1.33), the GPC peak was found to return back to the lower region. Additionally, based on two-dimensional (2-D) DOSY 1H NMR technique, the diffusion coefficients (D) of polymers 8, 9, and 10 were determined to be D = 3.98 × 10^{-10} m^2 s^{-1}, D = 19.95 × 10^{-10} m^2 s^{-1}, and D = 10.00 × 10^{-10} m^2 s^{-1}, respectively (Figures S8, S10, and S11). In terms of results, the diffusion coefficient of the linear polymer was much larger than those of the star polymers, indicative of a smaller hydrodynamic radius for the linear polymer, which agreed with the change tendency of hydrodynamic radius obtained from GPC investigation experiment.

With the success of multistep supramolecular transformations of metallacycle-linked polymers triggered by phosphine ligand-exchange reaction, the physical property regulation of different polymers was expected. The viscosity measurement was then conducted to verify the difference in intrinsic viscosity among the polymers 8, 9, and 10. Figure 3b shows the Huggins plots of different polymers. For star polymers 8 and 10, the [η] values were determined to be 0.123 and 0.110 dL/g, respectively, while the [η] value of the linear polymer 9 was found to be 0.085 dL/g, which was lower than that of the star polymers. Usually, the intrinsic viscosity value of a polymer with a large molecular weight is higher than those of the ones with small molecular weight. The occurrence of supramolecular transformation from six-armed star polymer to the linear one resulted in a significant decrease in molecular weight. Thus, the linear polymer 9 featured a lower intrinsic viscosity compared with the star polymers 8 and 10. The change of intrinsic viscosity again supported the realization of multistep supramolecular transformation of metallacycle-linked polymers.

Considering the crystalline nature of PCL polymer, 14 crystallization behaviors of the resultant polymers were then investigated by using differential scanning calorimetry (DSC). Figure 4a shows the melting curves of different polymers, from which the resulting polymers displayed the similar melting temperatures T_m around 50.0 °C. Meanwhile, the crystallization temperatures T_c of polymers 8, 9, and 10 were determined to be 8.02, 21.08, and 25.02 °C, respectively, according to the cooling curves as shown in Figure 4b. Moreover, polarized optical microscopy (POM) was employed to study the real-time crystallization processes for the resulting polymers. Figure 5 shows the polarizing optical photomicrographs of the resultant polymers at 30 °C at different time. It was found that a number of small granular objects with the stronger birefringence formed at the initial stage for 8 and 9. As time went on, the size of small spherulites gradually increased. After 10 min, the larger spherulites with diameters of 60 and 120 μm were observed for 8 and 9, respectively, and they filled the whole space gradually. Notably, during the same
crystallization time, the spherulites of linear polymer 9 showed a larger size compared with the star polymer 8, which indicated that the star polymer 8 displayed a relatively slower growth rate than that of the linear polymer 9. Interestingly, different from polymers 8 and 9, the star polymer 10 featured crystalline morphology with much larger sizes, which thus inspired our interest in mechanism investigation.

**Mechanism Investigation on Crystalline Behaviors of Different Metallacycle-linked Polymers.** According to the aforementioned study as shown in the previous section, the successive architectural transformations of three metallacycle-linked polymers driven by simple phosphine ligand-exchange reaction were confirmed. GPC elution time and the intrinsic viscosity clearly demonstrated that the star polymer 10 exhibited very similar properties to the starting star polymer 8 after the architectural transformation from the linear polymer 9. However, one may find that the crystallization behaviors of metallacycle-linked polymers sharing the same architecture, i.e., 8 and 10, were quite different from each other. This phenomenon indicated that not only architecture contributed significantly to the crystallization property of metallacycle-linked star polymers 8 and 10 in this study. Notably, these two polymers indeed shared the same architecture, while the only difference between them came from the phosphine ligands on the metallacycles due to the ligand exchange process. Thus, it was reasonable to attribute such crystallization behavior difference to the contribution of trivial ligand exchange from PPh3 to PEt3.

**Figure 5.** Real-time polarized optical microscopy photos of polymers 8–10 at 30 °C (scale bar = 100 μm): (a) 4 min, (b) 6 min, and (c) 10 min.

**Figure 6.** Simulation results of the self-assembly behaviors of metallacycles 5, 6, and 7 as well as the metallacycle-linked polymers 8, 9, and 10. Typical equilibrium snapshots of the assembled structures of 5, 6, and 7 (a), 8, 9, and 10 when the degree of polymerization of PCL is 20 (c), and 8, 9, and 10 when the degree of polymerization of PCL is 40 (e). Panels (b), (d), and (f) give the averaged interaction energy (per metallacycle) in corresponding cases.
To provide the physical insights into the architecture effect and even the very interesting ligand-exchange effect, coarse-grained molecular dynamics simulations were then applied to investigate the aggregation process of the metallacycles/metallacycle-linked polymers (see details of the simulation modeling in Figure S13). The self-aggregation of metallacycles without PCL (i.e., 5, 6, and 7) was first studied. As shown in Figure S14, with the time increased, these metallacycles self-assembled into small aggregates due to the π−π stacking between the metallacycles. However, because of the existence of the more remarkable steric hindrance between the individual metallacycles in the cases of 5 and 6, no further packing was observed (Figure 6a). On the contrary, due to the effective π−π stacking in the case of 7 (Figure 6b), the small aggregates could further form 2-D layered structures, indicating that the π−π stacking contributed much more than that of 5 and 6 during the aggregation process.

With this in mind, we then investigated the aggregation behaviors of the corresponding metallacycle-linked polymers (i.e., 8, 9, and 10) with PCL polymer chains. Polymeric chains with different polymerization degree (DP = 20 or 40) were chosen for the simulation study. As shown in Figure 6c and Figure S15, due to the PCL chain interaction, all of the metallacycle-linked polymers with the degree of polymerization of PCL of 20 could self-assemble into the large structures. However, the final structures were different. For instance, in the cases of polymers 8 and 9, they preferred to form the micelle-like structures due to the weaker π−π stacking between the metallacycle cores (Figure 6d), while for 10, apart from the PCL interaction, the π−π stacking between the metallacycle scaffold also contributed to the self-assembly process. As a result, similar to the corresponding metallacycle 7, 2-D layered aggregation was afforded in the case of polymer 10. With the further increase of the degree of polymerization of PCL from 20 to 40, due to the enhanced PCL interactions, the role of π−π stacking in the self-assembly processes could be weakened, and the large-scale 2-D structure could not be observed in the case of 10 (Figure 6e,f). Nevertheless, there still existed some layered or packed structures in the final aggregation structure of 10, which were scarcely found in the cases of 8 and 9 (Figure S16). It is worth mentioning that, although DP = 20 of PCL gave more significant difference between 7, 8, and 9 than the case of DP = 40, the same trend was also observed for the latter in the simulation study. In addition, according to the interaction energy shown in Figure 6b,d,f, the π−π stacking between the metallacycle 7 and the corresponding polymer 10 was stronger than the other two metallacycles and the corresponding polymers. These results again indicated that the decrease of steric hindrance of the metallacycle cores during the self-assembly processes might result in much more regular packing of the metallacycle, which thus dramatically increased the crystallization ability of the star polymer with the same metallacycle backbone and same architecture.

**CONCLUSION**

In summary, starting from a functionalized metallacycle constructed via coordination-driven self-assembly as the initiator, postassembly polymerization led to the successful synthesis of a new family of metallacycle-linked star polymers. By taking advantage of the facile structural conversion of trans-platinum acetylde moiety triggered by simple phosphine ligand-exchange reactions, the first example of successive supramolecular transformation (“from star polymer to linear polymer and then back to another star polymer”) of metallacycle-linked polymers was realized. More importantly, such supramolecular transformation gave rise to different polymers with the regulated physical and crystallization properties. Coarse-grained molecular dynamics simulations proved that the rigid metallacycles played an important role in determining the physical and chemical properties of the resultant star polymers. Considering the fact that the structure of polymers often plays an important role in determining their properties and applications, this study provides not only a novel and facile approach for effective successive supramolecular transformation of polymers but also a practical strategy for the construction of novel stimuli-responsive materials based on the strategy of supramolecular transformation.

**ASSOCIATED CONTENT**

Supporting Information

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Synthesis, characterization, and other experimental details (PDF)

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**Notes**

The authors declare no competing financial interest.

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