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Switching of the conformational flexibility of a diazacyclooctane-containing ladder polymer by coordination and elimination of a Lewis acid

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A recently developed diazacyclooctane-containing ladder polymer, which represents the first example of a ladder polymer with a large degree of conformational freedom, undergoes coordination and elimination of a Lewis acid (BPh_2Cl), leading to reversible switching of the conformational flexibility of the polymer backbone. By taking advantage of this behaviour, it may be possible to control the bulk properties of the ladder polymer.

Ladder polymers with multiple bonds in their main chains generally show excellent thermal and chemical stability.^{1–16} Although all existing examples of structurally well-defined ladder polymers feature a rigid main chain with a limited degree of conformational freedom, we recently reported the first example of a conformationally flexible ladder polymer.¹⁷ The successful synthesis of this ladder polymer relies on the post-polymerization reaction of a Tröger's base-containing ladder polymer (TB-ladder polymer), which was developed by McKeown and coworkers.^{11–13,16} The Tröger's base (TB) skeleton of the TB-ladder polymer (Fig. 1a), upon *N*-methylation and subsequent hydrolysis, was transformed into a diazacyclooctane (DACO) skeleton,^{17–20} to afford a diazacyclooctane-containing ladder polymer (DACO-ladder polymer), which exhibits ring-flipping motion (Fig. 1b).¹⁷ The resulting DACO-ladder polymer (*i.e.*, poly-1, Scheme 1) has two adjacent amino groups in the conformationally flexible ring, thereby allowing the reconstruction of a rigid bicyclic ring through bidentate coordination using proper Lewis acids. Since such a Lewis acid/base complexation usually occurs reversibly, this process could make it possible to control the conformational flexibility of poly-1. Here we show the reversible formation of rigid bicyclic and flexible monocyclic structures in the main chain of poly-1 through coordination and elimination of diphenylchloroborane (BPh_2Cl) on the amine functionalities (Fig. 1b).

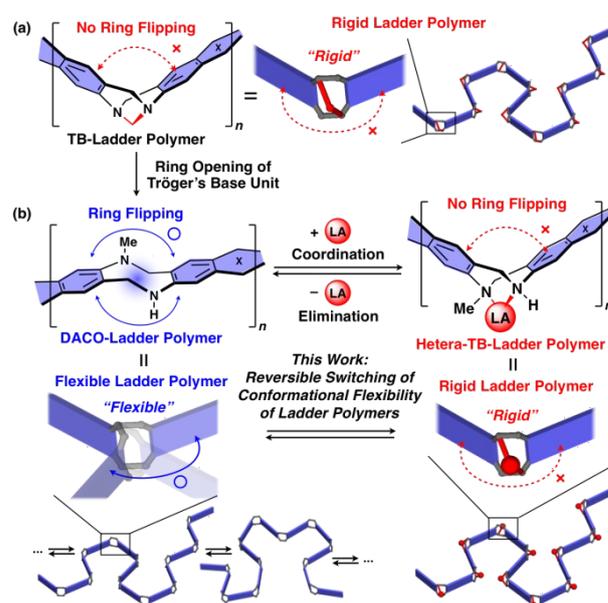
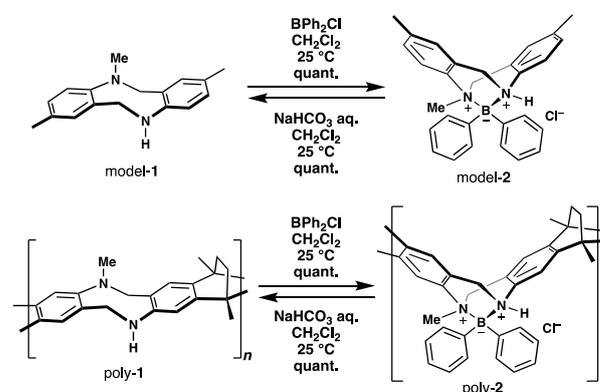


Fig. 1. The structural transformation of ladder polymers. Schematic structures of (a) a TB-ladder polymer with a covalent bicyclic Tröger's base skeleton and (b) a DACO-ladder polymer with a conformationally flexible monocyclic skeleton or a coordinate bicyclic skeleton, each of which is interconvertible through coordination and elimination of a Lewis acid.



Scheme 1. Schematic illustrations of the reversible structural transformations in a model compound (model-1) and poly-1 upon coordination and elimination of BPh_2Cl .

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Prior to the investigation of the structural transformation of poly-1, we examined the coordination behaviour of a model compound (model-1)^{17–20} (Scheme 1), which allowed a detailed structural assessment using NMR techniques. DACO derivatives are known to undergo coordination of transition metal ions (Co, Cu, Ni, Zn, Pd, Pt) to give 1:2 complexes, where one metal ion is sandwiched by two DACO molecules.^{21–24} In the present study, we chose diphenylchloroborane (BPh₂Cl)²⁵ as a Lewis acid, since the chloro group of BPh₂Cl is expected to be replaced by nitrogen of the secondary amino group of the DACO unit, while further coordination that results in sandwich-type complexes can be suppressed due to the steric hindrance of the two phenyl groups on boron. In fact, high-resolution APCI mass spectrometry of a 1:1 mixture of model-1 and BPh₂Cl in CH₂Cl₂ clearly showed an ion peak of $m/z = 417.2500$ and an isotopic pattern (Fig. S1, ESI⁺), which agreed with those

expected for [model-2-Cl]⁺ (calcd. for C₂₉H₃₀BN₂⁺: $m/z = 417.2502$).

When 1 equivalent of BPh₂Cl was added to a CDCl₃ solution of model-1 at 25 °C, the NMR signals of model-1 immediately changed (Figs. 2–4, Figs. S2–S8, ESI⁺). The resultant spectral patterns indicated the formation of model-2 (Scheme 1) through a 1:1 coordination of BPh₂Cl to model-1. Thus, in the ¹H NMR spectrum (Fig. 2b), the signal arising from the protons of the *N*-Me (*j*) and *N*-H groups (*k*) appeared at downfield regions with chemical shifts of 3.74 and 12.1 ppm, respectively. Likewise, the ¹H NMR signals (*a*) and (*c*), which are assignable to the aromatic protons at the *ortho*-position relative to nitrogen, showed a significant downfield shift (8.12 and 8.53 ppm). Based on these observations, both nitrogen atoms of the DACO ring are positively charged upon coordination of BPh₂Cl.^{26,27} Consistently, in the ¹³C NMR

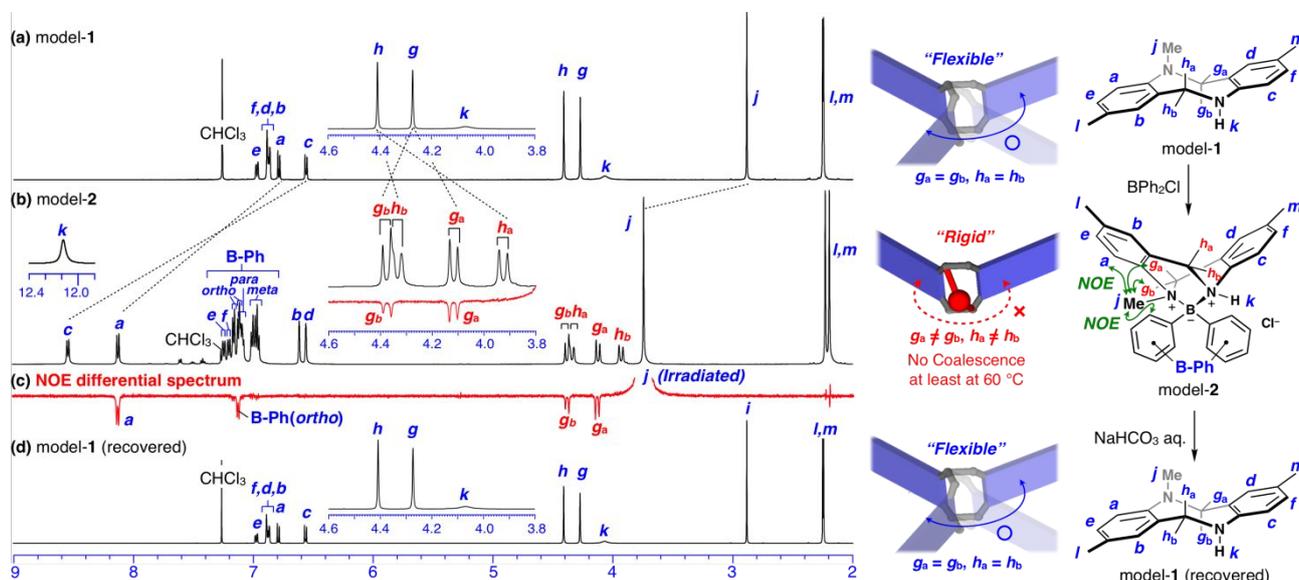


Fig. 2. ¹H NMR spectra (500 MHz) of (a) model-1, (b) model-2 and (d) recovered model-1 in CDCl₃ at 25 °C, and (c) NOE differential spectrum of model-2 upon irradiation of proton *j* in CDCl₃ at 25 °C.

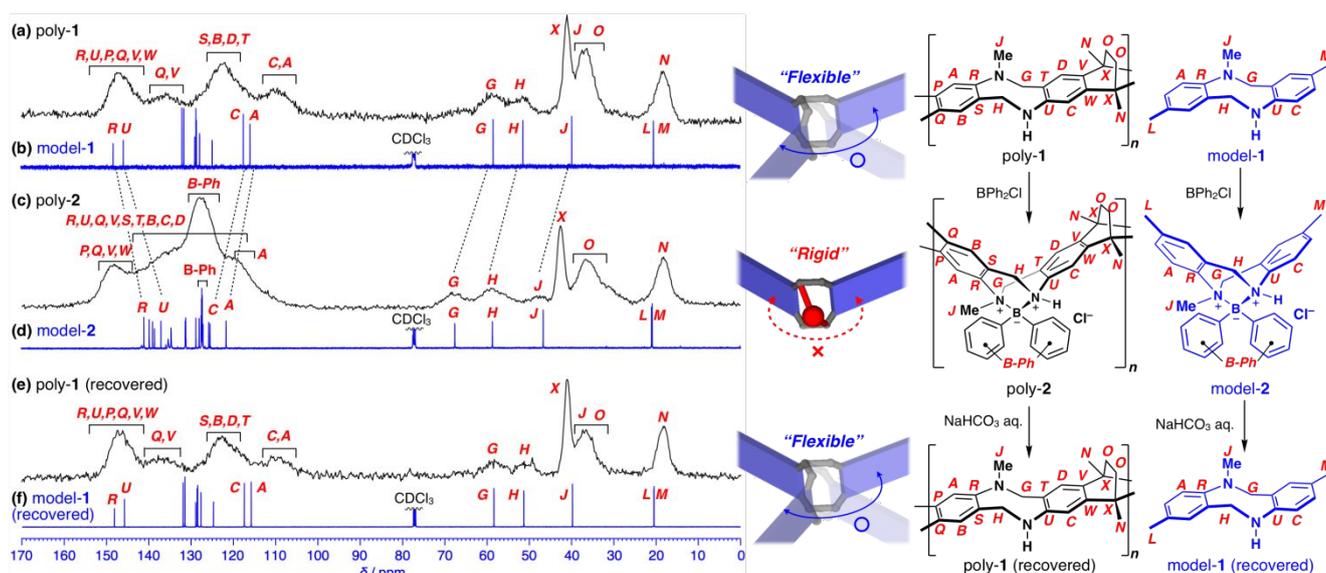


Fig. 3. ¹³C NMR spectra of (a) poly-1, (b) model-1, (c) poly-2, (d) model-2, (e) recovered poly-1, and (f) recovered model-1 (100 MHz solid-state CP-MAS at 25 °C for poly-1 and poly-2; 125 MHz in CDCl₃ at 25 °C for model-1 and model-2).

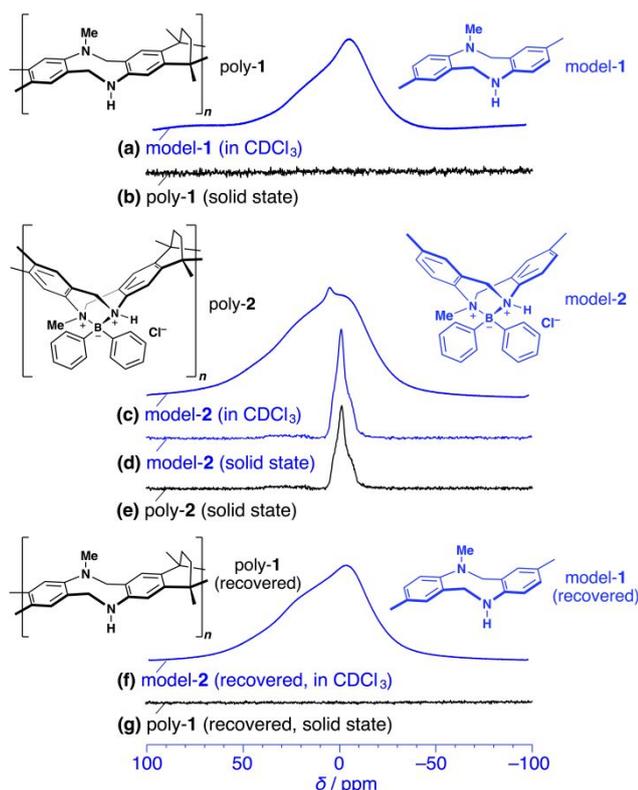


Fig. 4. ^{11}B NMR spectra of (a) model-1, (b) poly-1, (c) model-2 (in CDCl_3), (d) model-2 (solid state), (e) model-2, (f) recovered model-1, and (g) recovered poly-1 (128 MHz solid state CP-MAS, at 25 °C for poly-1, model-2 and poly-2, 160 MHz, in CDCl_3 , at 25 °C for model-1 and model-2). The broad peaks in the region from 50 to -40 ppm are the contributions from a borosilicate-glass NMR tube.

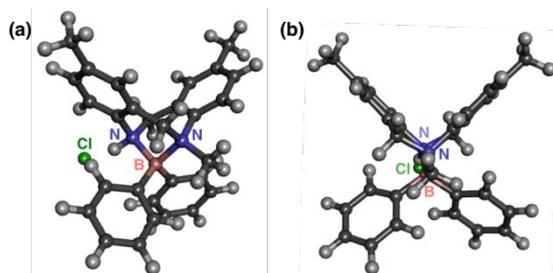


Fig. 5. (a) Perspective and (b) side views of the optimized structure of model-2 at the B3LYP/6-31G(d) level of theory (see experimental section and ESI[†] for further details).

spectra in CDCl_3 (Fig. 3b,d), the signals arising from the carbons (G), (H) and (J) bonded to the nitrogen atoms displayed a downfield shift. Furthermore, a nuclear Overhauser effect (NOE) was observed between the *N*-Me proton (*j*) and *ortho*-protons of the phenyl group on boron (Fig. 2c, Fig. S4, ESI[†]), meaning that these groups are in proximity to each other. According to the optimized structure of model-2 (Fig. 5) simulated by density functional theory (DFT) calculations, the closest distance between the *N*-Me proton (*j*) and *ortho* proton of phenyl group on boron is 2.05 Å, which is short enough to exhibit an NOE correlation (Fig. 2c). Therefore, the

nitrogen atom of the *N*-Me group coordinates to the boron atom to form a boron-bridge DACO ring (Scheme 1). We also measured the ^{11}B NMR spectra (Fig. 4a,c) of model-1 and a 1:1 mixture of model-1 and BPh_2Cl in CDCl_3 . While the ^{11}B NMR signal of BPh_2Cl was observed at 63 ppm, it was highly upfield-shifted upon mixing with model-1 and was observed at 4.5 ppm, which is characteristic of negatively charged four-coordinated boron atoms.^{25,28} The FT-IR spectrum of model-2 showed multiple peaks in a region of 2600–2200 cm^{-1} , as typically observed for *N*-H stretching vibration of tertiary ammonium salts (Fig. S9, ESI[†]). All of the spectroscopic observations fully support the formation of model-2 featuring a bicyclic structure by the bidentate coordination of the boron atom to two nitrogen atoms of the DACO skeleton (Scheme 1).

When 0.5 equivalents of BPh_2Cl were reacted with model-1, the signals of model-1 and model-2 were observed separately (Fig. S10, ESI[†]). Hence, the complexation of BPh_2Cl and model-2 is strong, and a fast exchange of the BPh_2Cl moiety in model-2 with remaining model-1 does not occur. We also found that the presence of the secondary amino group on the DACO ring is essential for the bidentate coordination of BPh_2Cl , because a DACO derivative with two tertiary amino groups did not undergo coordination of BPh_2Cl (Fig. S11, ESI[†]).²⁹

^1H NMR spectroscopy provided information about the change in the degree of conformational freedom and structural symmetry upon complexation. The protons on the same *N*-methylene carbons (*g*) and (*h*) of the DACO ring of model-1 (Fig. 2a) were observed equivalently, meaning that the coordination-free DACO undergoes a rapid ring-flipping. In contrast, the corresponding protons (*g*) and (*h*) in model-2 (Fig. 2b) were observed separately as (*g*_a), (*g*_b), (*h*_a) and (*h*_b), similar to the case of Tröger's base derivatives¹⁷ with a rigid covalent bridge. Obviously, the ring-flipping motion of the DACO ring is sufficiently suppressed upon coordination of BPh_2Cl . Since the signals of (*g*_a), (*g*_b), (*h*_a) and (*h*_b) of model-2 did not show any coalescence upon heating at 60 °C (Fig. S12, ESI[†]), the conformational rigidity of model-2 can be maintained at a high temperature. When the CH_2Cl_2 solution of model-2 was treated with a 5% aqueous NaHCO_3 solution, the coordinated BPh_2Cl was released from the DACO ring, resulting in the quantitative recovery of model-1, which exhibits rapid ring-flipping (Figs. 2d, 3f, 4f). Therefore, the conformational flexibility of the DACO ring can be switched by the coordination and elimination of BPh_2Cl .

With the above results for model-1 in mind, we investigated the conformational behaviour of poly-1 (Figs. 3a, 4b, Figs. S13–S17, ESI[†], $M_n = 5.4 \times 10^4$ Da), which was prepared by the procedures reported previously (Scheme 1).¹⁷ Addition of BPh_2Cl (0.21 mmol) to a CH_2Cl_2 solution of poly-1 (0.21 mmol) at 25 °C gave rise to an insoluble substance, probably due to the polyionic nature of the resulting coordinated polymer (poly-2, Scheme 1). Thus, we characterized the structure of poly-2 using solid-state ^{13}C and ^{11}B NMR CP-MAS (cross polarization magic angle spinning) spectroscopy (Figs. 3c, 4d). Poly-2 displayed ^{13}C NMR signals at 68.59 and 48 ppm, which agree well with those of the carbons (G), (H) and

(J) of model-2 (Fig. 3c,d). In the solid-state ^{11}B NMR, model-2 and poly-2 both showed a signal at around -1.5 ppm (Fig. 4d,e) arising from four-coordinated boron.^{25,28} The FT-IR spectrum of model-2 showed quite broad peaks in the region of $2600\text{--}2200\text{ cm}^{-1}$ due to N-H stretching vibration of the tertiary ammonium salts (Fig. S9, ESI[†]). These observations clearly indicate that the quantitative coordination of BPh_2Cl to the DACO ring at the monomer level also occurs successfully in the polymeric system, which involves the transformation of a conformationally flexible monocyclic ring structure to a rigid boron-bridged bicyclic ring structure. We confirmed that a treatment of a solution of poly-2 in CH_2Cl_2 with a 5% aqueous NaHCO_3 solution allows quantitative recovery of poly-1 (Figs. 3e, 4g). Since the molecular weight of recovered poly-1 ($M_n = 5.3 \times 10^4$ Da, Fig. S17, ESI[†]) was almost identical to that obtained for as-prepared poly-1 ($M_n = 5.4 \times 10^4$ Da), bond-breaking of the main chain, resulting in a decrease in M_n , did not occur during the coordination and elimination of BPh_2Cl .

Conclusions

We have described the first system of ladder polymers capable of interconversion between rigid and flexible conformations. The key for this achievement is the use of a conformationally flexible DACO-containing ladder polymer (Fig. 1b),¹⁷ which possesses two nitrogen atoms that provide a Lewis base site at the appropriate positions for bidentate coordination of a Lewis acid. As clearly demonstrated with a model compound (model-1), bidentate coordination and hydrolytic removal of BPh_2Cl for the DACO ring that accompany the formation of a rigid bicyclic structure and recovery of flexible monocyclic structure, respectively, occurs quantitatively. The switching of conformational flexibility based on this DACO ring-shape modification could be applied to poly-1. This finding offers an opportunity to design new stimuli-responsive ladder polymers. Studies along these lines are underway in our group.

Conflicts of interest

There are no conflicts to declare.

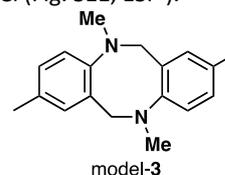
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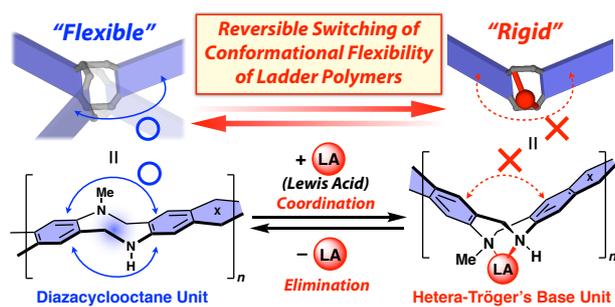
Technical Department, Tokyo Institute of Technology, for their support with the NMR and SEC-MALS measurements.

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- Tröger's base derivatives with two quaternized nitrogen atoms have been reported.²⁷
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- The ^1H NMR spectrum of model-3¹⁸ did not change upon the addition of BPh_2Cl (Fig. S11, ESI[†]).



Graphical Abstract



We report the first system of ladder polymers capable of interconversion between rigid and flexible conformations by coordination and elimination of a Lewis acid (BPh₂Cl) on diazacyclooctane units in the main chain.