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A Mortise-and-Tenon Joint Inspired Mechanically Interlocked Network

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Abstract: Mortise-and-tenon joints have been widely used for thousands of years in wooden architectures in virtue of their artistic and functional performance. However, imitation of similar structural and mechanical design philosophy to construct mechanically adaptive materials at the molecular level represents a challenging goal. Herein, we report a mortise-and-tenon joint inspired mechanically interlocked network (MIN), in which the [2]rotaxane crosslink not only mimics the joint in structure, but also reproduces its function in modifying mechanical properties of the MIN. Benefiting from the hierarchical energy dissipative ability along with the controllable intramolecular movement of the mechanically interlocked crosslink, the resultant MIN simultaneously exhibits notable mechanical adaptivity and structural stability in a single system, as manifested by decent stiffness, strength, toughness, and deformation recovery capacity. The present research provides a structurally mimetic strategy toward mechanically robust yet dynamic mechanically interlocked polymers, which will facilitate the progress and application of mechanically interlocked molecules in intelligent materials.

Introduction

Over the last century, crosslinked polymer networks have played essential and ubiquitous roles in a wide range of fields owing to their attractive mechanical properties.^[1] Depending on the nature of the crosslinks, the polymer networks could be classified into covalent polymer networks (CPNs) and supramolecular polymer networks (SPNs), wherein the former features permanent crosslinks (Figure 1a) and the latter possesses dynamic crosslinks (Figure 1b).^[2] Generally, CPNs exhibit mechanical robustness but lack of dynamic property.^[3] In contrast, while dynamic crosslinks could endow SPNs with reversible stimuli-responsiveness, they have also affected the stability and strength of the networks.^[4] As such, the development of novel polymer networks with integrated dynamic stability and mechanical adaptivity has been a long-standing pursuit of chemists and materials scientists, although it still remains a significant challenge.

In ancient wooden buildings, the mortise-and-tenon joint has been widely used due to its combination of remarkable strength and durability, simplicity, as well as the elegance of its appearance.^[5] In addition, because the mortise and tenon are joined physically, the joint brings both dynamic and robust features to the architecture and the features could be further modulated by a wedge (Figure 1c).^[6] By virtue of these merits, wooden buildings oftentimes showcase great seismic performance. Inspired by the elegant structure, we envision that polymer networks with crosslinks resembling the mortise-andtenon joint may simultaneously combine the mechanical robustness and stability of CPNs as well as dynamic and responsive features of SPNs. However, the joint-like crosslinks are quite rare on account of their complicated and delicate topological structures along with the inherent adaptive properties.

[2]Rotaxanes, one of the most basic constituents of mechanically interlocked molecules (MIMs), involve one wheel on a dumbbell shaped axle.^[7] The fascinating topological structure allows for controllable intramolecular movement of the interlocked components but still keeps structural integrity. As such, they have found promising applications in a variety of areas such as interfacial cargo delivery, precise synthesis of biomolecules, and artificial molecular machines.^[8] Particularly, the [2]rotaxane is structurally similar to the mortise-and-tenon joint, in which the wheel resembles the mortise, the axle resembles the tenon, and the recognition site on the axle resembles the wedge that is able to stabilize the delicate structure. Along this line, [2]rotaxanes would be a great candidate for the design of our expected polymer networks.

Herein, we report a mortise-and-tenon joint inspired mechanically interlocked network (MIN) which well integrates dynamic stability and mechanical adaptivity in a single system, and thus exhibits attractive mechanical properties (Figure 1c). Specifically, the dibenzo-24-crown-8 (DB24C8) wheel is able to be pulled away from the thermodynamically favored recognition site of the dibenzylammonium salt (DBAS) under tension, thereby endowing the MIN with dynamic behavior and energy dissipation ability. At the same time, the mechanical bond not only links the constituents together in a similar manner that covalent bond does, but also shows mechanical strength comparable to the covalent counterpart,^[9] which would thus guarantee mechanically robust and stable properties of the MIN.

Results and Discussion

To demonstrate our design, we chose DB24C8 and DBAS as the complementary host-guest pair to construct tetraolefin [2]rotaxane **1** (Scheme S1).^[10] Photo-induced, radical-mediated thiol-ene click chemistry was employed to prepare the mechanically interlocked network (MIN-**1**) (Figure 1c). As a comparison, we also constructed a "wedge-free" [2]rotaxane **2** via

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Figure 1. Schematic representation of the three types of polymer networks. a) Covalent polymer network with permanent crosslinks. b) Supramolecular polymer network with dynamic crosslinks. c) The mortise-and-tenon joint inspired design and preparation of polymer network with mechanically interlocked crosslinks.

N-acetylation of the sec-ammonium salt moiety of the [2]rotaxane $1^{[11]}$ followed by the same thiol-ene click reaction to generate MIN-2 (Scheme S1).

We firstly employed ¹H NMR measurement to prove the preparation of the [2]rotaxane monomers (Figures S21 and S24). Partial ¹H NMR spectra of DB24C8 wheel, [2]rotaxane 1, and DBAS axle are shown in Figure 2. Upon the formation of [2]rotaxane 1, the aromatic protons of H₂, H₃, and ethyleneoxy protons H₅₋₇ on the DB24C8 wheel as well as protons H_c and H_d of the DBAS axle shifted upfield. Meanwhile, the methylene protons He experienced downfield shift. These observations originated from the combination of the macrocyclic shielding effect and [N-H-O] and [C-H-O] hydrogen bonds. In addition, the appearance of protons H_a on the triazole units and H_b on the m-xylene stoppers confirmed the success of the stoppering reaction. After treating [2]rotaxane 1 with acetic anhydride and trimethylamine, the neutral and asymmetric [2]rotaxane 2 was generated, which was proved by the complicated and split NMR proton signals (Figure S27). These two [2]rotaxanes were also ascertained by ¹³C NMR spectra (Figures S22 and S25) and electrospray ionization mass spectrometry (ESI-MS) (Figures S23 and S26). Then, we employed the two [2]rotaxanes as mechanically interlocked crosslinks to construct the MINs via thiol-ene chemistry, and the completion facile of photopolymerization was confirmed by fourier transform infrared spectroscopy (FT-IR) (Figure S28). The swelling experiments of the MINs further indicated the formation of crosslinked networks (Figure S29).

After the preparation of MINs, we investigated their thermal properties. Thermal gravimetric analysis (TGA) exhibited that the decomposition temperatures of both MIN-1 and MIN-2 were higher than 250 °C, indicating good thermal stability (Figure S30). The differential scanning calorimetry (DSC) of the two samples were also conducted and the glass transition temperature (T_g)

values were measured to be 30 and 24 °C for MIN-1 and MIN-2, respectively (Figure 3a). We inferred that the distinction between the T_g values could be attributed to the suppressed degree of freedom of the polymer framework enabled by the host–guest recognition, which behaved like a wedge stabilizing the mortise-and-tenon joint. Moreover, dynamic mechanical analysis (DMA) was carried out to discriminate the thermomechanical behaviors of MINs. As shown in Figure 3b, the storage modulus (E') of MIN-1 was higher than that of the MIN-2, which was also ascribed to the contribution of the host–guest recognition. Moreover, after



Figure 2. Partial ¹H NMR spectra (400 MHz, CDCl₃, 298 K) of a) DB24C8 wheel, b) [2]rotaxane 1, and c) DBAS axle.

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undergoing glass transition, the MINs still exhibited pronounced plateaus and their E' values were much larger than those of loss moduli (E''), suggestive of good elastic behaviors and thermomechanical stability of the networks.

Furthermore, we studied the wedge effect of the crosslinks on the mechanical properties of the MINs via tensile tests. As shown in Figure 3c and d, MIN-1 was found to exhibit favorable mechanical performance including higher stiffness (Young's modulus = 246 MPa), strength (maximum stress = 15.5 MPa), and toughness (12.9 MJ/m³) than those of the MIN-2 (Young's modulus = 145 MPa, maximum stress = 9.95 MPa, and toughness = 7.40 MJ/m³). Just like the fixing function of the wedge in the mortise-and-tenon joint, the host-guest recognition in crosslinks made an improvement in the mechanical features of the MINs. Moreover, there is no obvious difference in terms of fracture strain of the MIN-1 (106%) and MIN-2 (108%) (Figure 3c). The comparable results could be explained that these two MINs have very similar network structures.



Figure 3. a) DSC curves of MIN-1 and MIN-2 recorded by the second heating scan from -40 to 100 °C with a heating rate of 20 °C/min. b) DMA curves of the MINs recorded during the heating process from -35 to 100 °C with a heating rate of 5.0 °C/min. c) Stress-strain curves of MIN-1 and MIN-2 recorded with a stretching rate of 100 mm/min. d) Young's moduli and toughness of MIN-1 and MIN-2 calculated based on their stress-strain curves.

The above results have revealed that the host-guest interaction could stabilize the mechanically interlocked crosslinks and thus make them more robust. In essence, the host-guest recognition is also dynamic and reversible because of its noncovalent nature. To clarify this issue, a series of measurements were performed. The results of stress relaxations were shown in Figure 4a. Under different strains (3%, 5%, and 10%), similar stress-relaxation behaviors were observed: the stress dropped rapidly in the initial part of the test followed by a gradual relaxation at a longer time. In addition, the stress relaxation decreased as the strain increased, namely, higher strain led to lower relaxation. The considerable stress-relaxation of MIN-1 might be related to the contribution of the dynamic mechanically interlocked crosslinks.

The dynamic character of the crosslinks was further revealed by cyclic tensile tests (Figure 4b). For different applied strains (from 10 to 60%), large hystereses were observed for MIN-1 after reloading, which implied remarkable ability in energy dissipation. It is worth noting that MIN-2 also exhibited pronounced hystereses under the same conditions (Figure S33). Force-induced sliding of the DB24C8 wheel could be responsible for the energy dissipation of the MIN-2, which would also occur in MIN-1 when the wheel is pulled away from the DBAS site.^[12] In addition, the hysteresis areas of the loading-unloading cycle of MIN-1 were larger than those of the MIN-2 with the same strains, reflecting the role of host-guest dissociation in energy dissipation (Figure 4c). Therefore, these results suggested that both the host-guest binding and intramolecular motion of the wheel on the axle contributed synergistically to the energy dissipation of MIN-1.

Then, we wondered what would happen after the DB24C8 wheel was slid away from the recognition site. To study this issue, we conducted cyclic tensile tests in which the MIN-1 was repeatedly loaded to a 40% strain and unloaded with different rest intervals ranging from 0 to 40 min (Figure 4d). The second circle without relaxing showed a much smaller hysteresis loop compared with the first one. Moreover, a large residual strain was also observed. The phenomena were related to the dissociation and movement of the DB24C8 wheel along the axle, but which could basically restore when the relaxing time was extended to 20 min. Compared with MIN-2, the recovery of MIN-1 was slightly faster because of the existence of host-quest interaction (Figures S34 and S35). Notably, although it was not as good as MIN-1, the deformation recovery of MIN-2 was comparable to most of the reported elastomers,^[13] which was probably due to the role of the stopper in restricting further movement of the DB24C8 wheel.



Figure 4. a) Stress relaxation curves of MIN-1 at different pre-stretched strains. b) Cyclic tensile test curves of MIN-1 with increased maximum strains. c) Hysteresis areas of MIN-1 and MIN-2 calculated from each circle of cyclic tensile test curves. d) Cyclic tensile test curves of MIN-1 loaded at a strain of 40% with rest intervals ranging from 0 to 40 min. e) Schematic illustration of possible sliding movement of the wheel on the axle under tension (left) and after the release of external force (right). *F* is the external force and *F* denotes the driving force of host–guest interaction.

Based on these results, we are able to deduce the working mechanism of the mechanically interlocked crosslinks in the MINs. On one hand, the dissociation of the host–guest recognition could

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be regarded as an effective pathway to dissipate external force (Figure 4e, left). And, once the DB24C8 wheel is pulled away from the DBAS site, its motion on the axle could further dissipate energy. Compared with CPNs, these dual dynamic properties endow corresponding MIN with good mechanical adaptability and unusual performance in energy dissipation. On the other hand, the *m*-xylene stopper could prevent the deslipping of the DB24C8 wheel from the axle, which is beneficial to the stability and deformation recovery capability of the MIN. Besides, host-guest interaction as a driving force could also contribute to the recombination of the dissociated wheel and axle. Hence, the MIN would exhibit a faster rehabilitation of the deformed network compared with general SPNs (Figure 4e, right). As such, the stability of the MIN can be described as follows: the mechanically interlocked crosslinks are stable under ambient conditions due to the host-guest complexation, and even if it dissociates under tension, the recovery of the crosslink is fast as a result of the synergistic effect between the stopper and host-guest recognition. Therefore, the mortise-and-tenon joint inspired mechanically interlocked crosslinks impart both dynamic stability and mechanical adaptability to the resultant MIN.



Figure 5. a) Dielectric loss spectra of MIN-1 and MIN-2 measured at -30 °C. b) Tensile behaviors of MIN-1 under different stretching rates. c) Fitting curve of yielding stress as a function of logarithm of strain rate. d) Creep and recovery behaviors of MIN-1 and MIN-2 at a constant stress of 0.5 MPa.

The hypothesized mechanism is based on the dissociation and recombination of the DB24C8 and DBAS recognition in the MIN, so it is necessary to understand such processes. To demonstrate the dissociation of the DB24C8 wheel from the DBAS recognition site under tension, dielectric relaxation spectroscopy (DRS) measurements were carried out. Since the host–guest dynamics of the MINs are quite sensitive to temperature, the dielectric relaxation was deliberately separated into two regimes, namely, above T_g and below T_g . At 50 °C (> T_g), we didn't observe the dielectric relaxation process for both MIN-1 and MIN-2 (Figure S36), which can be explained that the dielectric permittivity and loss were masked by strong direct current conductivity. We then turned to run the test at -30 °C (< T_g). As shown in Figure 5a, the dielectric loss spectrum of the stretched MIN-1 as a function of

frequency displayed a marked relaxation process. The molecular basis of the process lies in the motion of free ammonium groups, which were released by the dissociation of DB24C8 and DBAS under tension. By contrast, we couldn't observe similar dielectric relaxation behaviors on the samples of the unstretched MIN-1 as well as MIN-2 with or without being stretched (Figure 5a).

In order to get more information about the host-guest interaction in the mechanically interlocked joint, tensile tests with different stretching rates were performed. As shown in Figure 5b, the mechanical behaviors of the MIN-1 were highly dependent on the deformation rate, indicative of the involvement of dynamic and reversible host-guest interactions.[13b] Moreover, there was a linear relationship between the yielding stress and the natural logarithm of the strain rate, which was in accord with the Eyring model of external force induced dissociation of noncovalent bonds (Figures 5c).^[14] The apparent activation energy used to evaluate the energy barrier to overcome the mobile segments was calculated to be 17 kJ/mol. In addition, the activation volume extracted by data fitting was 3.4 nm³, which reflected the size of polymer segments involved in the motion associated with yielding. In general, structural changes of networks should be responsible for the yielding of elastomers. For MIN-1, the structural change is more likely due to the sliding motion of DB24C8 wheel on the DBAS axle. Therefore, we speculate that the energy to dissociate the host-quest recognition and launch the motion of DB24C8 wheel is about 17 kJ/mol.

The versatile roles of the mechanically interlocked crosslinks in MIN-1 could be further confirmed by the creep and recovery experiments (Figure 5d). At the initial stage (< 300 s), the creep rate of MIN-2 was much faster than that of MIN-1, and the curve of MIN-2 tended to level off. During this process, the motion of DB24C8 wheel in MIN-2 reached its equilibrium, but only basic deformation of the network occurred in MIN-1, indicating the wedge effect of host-guest recognition in stabilizing the network. After that, acceleration of creep was observed for MIN-1, which should be related to the gradual dissociation of host-guest recognition and followed by the sliding motion of the DB24C8 wheel. When stress was removed, the recovery of strain for MIN-1 was over 90% but that for MIN-2 was only 75%. As we mentioned above, such a notable recovery performance of MIN-1 was beneficial from the synergistic effect of the stopper and host-guest recognition. Therefore, the overall working process of the mechanically interlocked crosslink was well exhibited by the creep and recovery results, which further verified the proposed mechanism.

Conclusion

In summary, inspired by the mortise-and-tenon joint, we developed a mechanically adaptive yet structurally stable mechanically interlocked network (MIN) by means of facile thiolene click chemistry of the tetraolefin [2]rotaxane and 3,6-dioxa-1,8-octanedithiol. The sliding motion of the DB24C8 wheel on the axle under tension endowed the MIN with dynamic behaviours resembling SPNs. The unique interlocked structure of the mechanical bond further led to the MIN with robust features, which are comparable to CPNs. It is worth noting that energy dissipation stemming from the dissociation of host-guest recognition and consequential sliding motion of the DB24C8 wheel also contributed to the mechanical behaviors of the MIN. In addition,

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the MIN exhibited unusual deformation recovery performance benefiting from the synergy of host-guest interaction and steric effect of the stopper. Therefore, the MIN successfully combined the mechanical robustness and stability of CPNs as well as dynamic and responsive features of SPNs. We anticipate that the mortise-and-tenon joint inspired molecular design would enable encouraging applications of mechanically interlocked polymers as advanced functional materials, such as mechanically adaptive elastomers, anti-scratch coatings, and smart soft actuators.

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Keywords: mortise-and-tenon joint • host–guest chemistry • mechanically interlocked molecules • mechanical adaptivity • mechanically interlocked polymers

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We demonstrated that the delicate mortise-and-tenon joint was precisely mimicked to construct a mechanically interlocked network (MIN), which simultaneously integrates incompatible mechanical adaptivity, robustness, and dynamic stability in a single system.