

Ordered Chain-Entanglement Topology and Compressive Mechanical Response in Crystalline Dative B—N Polymers

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Electronic Supplementary Information

Abstract While the effects of chain entanglement on the mechanical properties of polymer systems have been extensively studied, it remains a major challenge to further clarify the deformation and motion of the entangled polymers at the molecular scale. Herein, one-dimensional and two-dimensional long-range ordered entangled polymers, along with a non-entangled control, are constructed by exploiting the bonding and extended conformations of dative B—N bonds in identical monomers to drive polymerization, thereby providing a powerful platform to investigate the evolution mechanism of chain entanglements under stress stimuli and their impact on the mechanical properties of materials. Combined mechanical measurements and density functional theory calculations reveal that polymer mechanics are not only profoundly influenced by the presence of chain entanglements but also strongly dictated by the specific entanglement topology. Compared with one-dimensional entangled polymers containing a limited number of intertwined chains, two-dimensional entangled polymers, in which numerous chains interweave within a planar network, demonstrate markedly enhanced resistance to deformation. This study elucidates the role of entanglements in the mechanical properties of polymers, providing new insights into the relationship between polymer entanglement structures and material performance.

Keywords Entangled polymers; Mechanical properties; Single crystals; Supramolecular chemistry

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INTRODUCTION

Chain entanglement is typically defined as the topological constraints formed by the interpenetration and interlacing of polymer chains in space, which can manifest as transient or quasi-permanent network junctions.^[1] As a ubiquitous structural feature, chain entanglement plays a crucial role in enabling specific functions and applications in polymeric materials.^[2–4] In recent years, inspired by its complex topological characteristics and the resulting mechanical adaptability, chain entanglement has been widely exploited in the molecular design of high-performance polymers to enhance their mechanical properties. From a mechanical perspective, entanglement nodes not only

act as key topological constraints that maintain the structural integrity of the polymer network, but also serve as effective units for stress transfer and dissipation, thereby alleviating local stress concentrations under external loading. Meanwhile, chain sliding and rearrangement endow the system with energy-dissipation capability, ultimately enhancing its toughness and resistance to mechanical failure.^[5–7] Currently, studies on entangled polymer systems are predominantly focused on amorphous materials (such as gels and elastomers, Scheme 1a).^[8–12] Among these disordered entangled polymers, a deeper investigation of the molecular-scale deformation and motion of entangled polymers is unfeasible, hindering the elucidation of the causal relationship between polymer entanglement and mechanical properties. Long-range-ordered crystalline entangled polymers hold promise as unique molecular-scale platforms for investigating polymer chain entanglement; however, this area remains largely unexplored to date.

The primary challenge stems from the inherent difficulty in precisely constructing long-range-ordered crystalline poly-

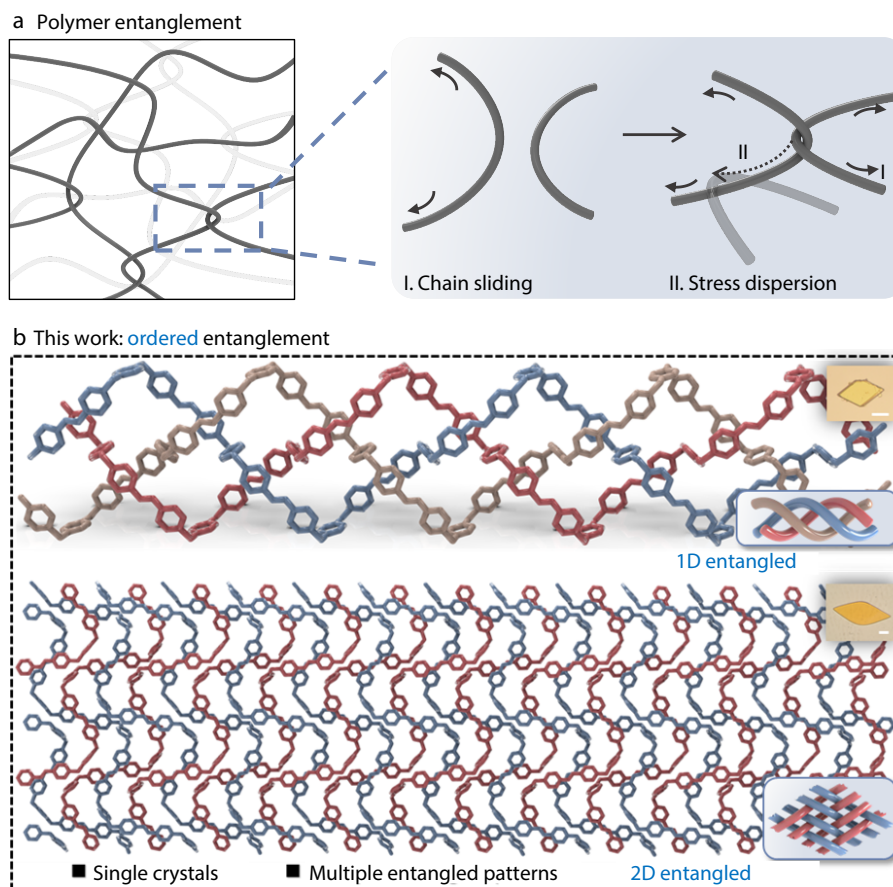
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Scheme 1 (a) Cartoon representation of disordered entanglements in amorphous polymer systems; (b) Ordered entanglements observed in the crystal structures of crystalline polymers **EP-1D** and **EP-2D** investigated in this work. The insets present optical images of **EP-1D** and **EP-2D** crystals, where the scale bars correspond to 20 μm .

mers, particularly within pure organic polymer systems.^[13–26] This complexity is further exacerbated when attempting precise synthesis of crystalline polymer systems with ordered entangled structures. Therefore, there is a pressing need to establish an appropriate research platform for crystalline entangled polymers to enable precise synthesis and characterization of polymer systems with highly ordered structures. Such a platform would provide essential insights into the evolution mechanism of chain entanglements under stress stimuli and their impact on the mechanical properties of crystalline polymer materials. Dative B–N bonding exhibits favorable dynamics in solution, facilitating adaptive self-correction during the formation of crystalline polymers, thereby promoting the establishment of long-range ordered structures.^[27–40] Moreover, the high conformational flexibility of this bonding allows the regulation of distinct chain entanglement forms under varying crystallization conditions, making it an ideal tool for investigating the mechanical properties of crystalline entangled polymers.

Herein, dative B–N bonding is utilized to drive polymerization, constructing one-dimensional (**EP-1D**) and two-dimensional (**EP-2D**) entangled^[38] polymers, as well as a control sample (**NEP**) devoid of entanglements, by manipulating the extension conformations of the dative B–N bonds using identical monomers, thereby establishing a robust research

platform for investigating the entanglement mechanisms of crystalline entangled polymers in terms of mechanical properties (Scheme 1b). Subsequent mechanical measurements revealed that **EP-2D** exhibited the best elasticity, followed by **EP-1D**, with **NEP** exhibiting the poorest elasticity. Additionally, DFT calculations indicated that the differences in the mechanical properties of these polymers arise from their distinct deformation pathways and the corresponding energy changes under different entanglement configurations. Specifically, compared to non-entangled polymers, one-dimensional entangled polymers can disperse and transfer stress through the slippage of the entanglement points. However, owing to the limited number of entangled chains (**EP-1D** consists of only three chains) and the confinement of stress transfer to a single dimension along the polymer chains, the mechanical properties were constrained when subjected to complex loads. In contrast, 2D entangled polymers are composed of numerous interwoven chains within a planar network, offering superior structural stability. Under stress, the polymer chains can adaptively slide, enabling stress to be effectively dispersed and transferred across the entire two-dimensional plane. Furthermore, the regulatory effects of solvents on the structure of entanglement points and their dynamics under applied stress were further investigated, aspects that have been less considered in previous studies on amorphous en-

tangled polymer systems. As a result, this structure can better maintain its stability under stress, preventing failure, and thus exhibiting superior mechanical performance. Therefore, this study investigated the influence of entanglements on the mechanical properties of polymers, providing a new observational perspective for understanding the relationship between polymer entanglement structures and material performance.

EXPERIMENTAL

Experimental details are included in the electronic supplementary information (ESI).

RESULTS AND DISCUSSION

Originally, **EP-1D** was obtained by heating a mixture of 1,4-bis(benzodioxaborole)benzene (**BDBB**) and 1,2-bis(4-pyridyl)ethylene (**BPE**) in toluene (Tol) at 70 °C for 24 h, followed by slow cooling to room temperature (Fig. 1a and Figs. S1–S4 in ESI). During the solvothermal reaction, polymerization and crys-

tallization occur simultaneously, giving rise to faint yellow single crystals (Scheme 1b). Uniformly distributed B and N elements were observed throughout the crystals, as revealed by energy-dispersive spectroscopy (EDS) mapping (Fig. S5 in ESI). Subsequently, single-crystal X-ray diffraction (SCXRD) was employed to directly analyze the precise molecular structure of **EP-1D** (Fig. 1b and Table S1 in ESI). The results revealed a triple-helical polymer with a spacing of 14.0 Å between the adjacent chains. The polymer's difficulty in crystallization led to spontaneous symmetry breaking in **EP-1D**, which, in turn, induced a helical conformation for each polymer chain. Remarkably, each polymer chain was repeated in a **R-Z-L** (**R**: right-handed, **Z**: Zigzag, and **L**: left-handed) manner, to ensure the chirality balance (Figs. S6 and S7 in ESI). Furthermore, given that in supramolecular polymerization, temperature and solvent served as pivotal factors in steering the polymerization pathways, we were inspired to delve deeply into the exploration of other entangled polymers.

By applying thermodynamic control, a 2D entangled polymer was obtained in Tol at an elevated temperature of 90 °C, namely **EP-2D** (Fig. 1c, Figs. S8–S10 and Table S2 in ESI). In

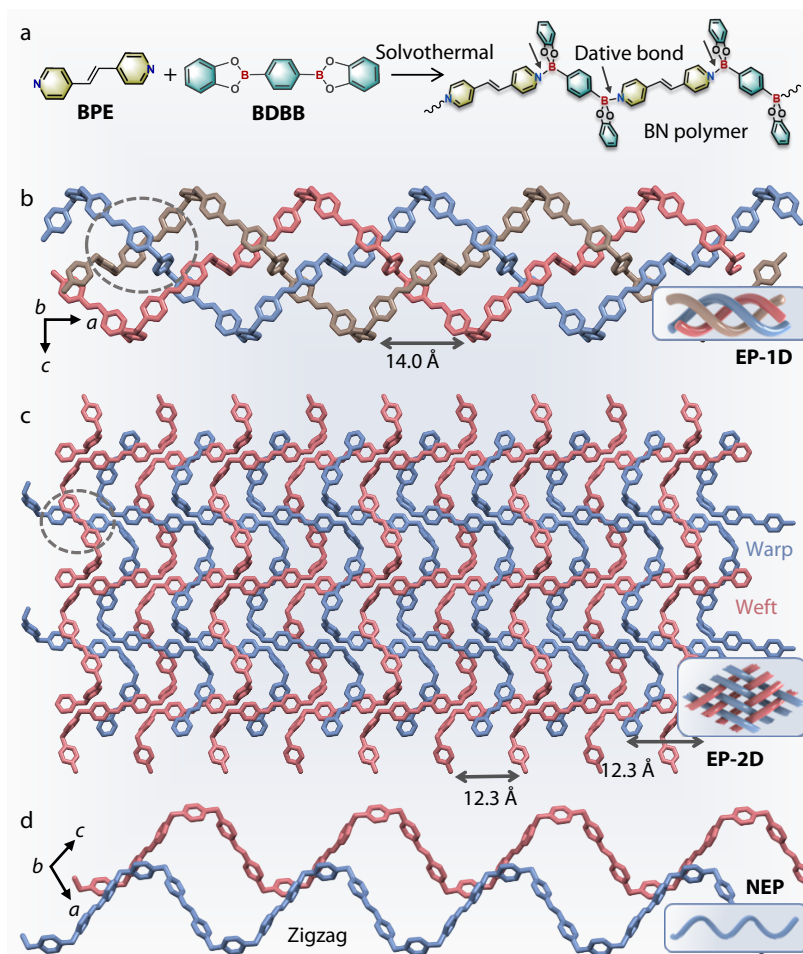


Fig. 1 (a) Chemical structures of monomers **BPE** and **BDBB**. Under solvothermal conditions, dative B—N bonds form to generate a polymer chain (BN polymer), which is further used to construct crystalline polymers **EP-1D**, **EP-2D**, and **NEP**; (b) Crystal structure of **EP-1D**, featuring a triple helical pattern. The interchain spacing of the triple helical structure is 14.0 Å. (c) Crystal structure of **EP-2D**, featuring a 2D entangled polymer network. The distance of the adjacent wefts (or warps) is 12.3 Å. (d) Crystal structure of **NEP**, characterized by a non-entangled pattern. H atoms and catechol groups have been omitted for the sake of clarity.

particular, molecular chains were categorized into warps and wefts (Fig. 1c), and chain entanglement occurred at the double bond positions when both the warp and weft chains shared the same chirality (Fig. S11 in ESI). Coincidentally, a non-entangled polymer (NEP, Table S3 in ESI) was obtained at 90 °C in *o*-dichlorobenzene (Fig. 1d), facilitating subsequent comparable mechanical studies. Overall, by adjusting the solvent and temperature, we obtained diverse patterns of chain entanglement using the same polymer threads.

As the core component responsible for the molecular chain movement and energy dissipation of entangled polymers, the configuration and stability of the entanglement nodes are crucial to the mechanical properties of polymers. For **EP-1D**, the 1D entangled polymers require internal solvents to maintain structural stability, thereby forming sandwich-like entanglement nodes that correspond to the kinetic species (Fig. 2a). Notably, the entanglement nodes in **EP-1D** were non-centrosymmetric, as evidenced by the pyridine-Tol distances of 6.11, 6.07, 3.68, and 3.67 Å, which may be due to the absence of inversion symmetry in interior Tol molecules. In **EP-2D** which exhibited a 2D entangled architecture, the solvent molecules adaptively moved from the interior to the exterior of the two polymer chains (Fig. 2b). This indicated the greater stability of the entanglement nodes in **EP-2D** compared to those in **EP-1D**, as a result of the stronger π - π interactions directly provided by the polymer chains, corresponding to the

thermodynamic species. To visually observe the intermolecular interactions, the non-covalent interactions (NCI) and reduced density gradient (RDG) distributions were calculated. Van der Waals interactions were found to be the majority NCI in the entanglement nodes of **EP-1D** and **EP-2D** (Figs. 2a and 2b), as revealed by the green spikes located around zero in the RDG analyses (Fig. S12 in ESI). Furthermore, larger areas of the green patterns were found in **EP-2D**, suggesting stronger intermolecular interactions. Specifically, when the solvent molecules migrated from the interior to the exterior of the two chains, the zero-point energy decreased by 23 kcal/mol (Fig. S13 in ESI). In the case of **NEP**, the polymer chains were fully solvated. This solvation was primarily driven by halogen interactions (38.3%), as quantified by the Hirshfeld surface analysis (Fig. S14 in ESI). Consequently, these solvent-polymer interactions hinder direct interaction and entanglement between the polymer chains themselves, leading to a zigzag configuration (Fig. 2c).

After the structures were established, these well-defined entangled polymers provided an ideal platform for elucidating the causal relationship between the polymer entanglement and mechanical properties. Subsequently, the mechanical performance of the three polymers was comparatively analyzed, and their respective characteristics were examined in detail. Owing to the intrinsic non-stretchability of these polymer crystals, nanoindentation tests remain the only viable al-

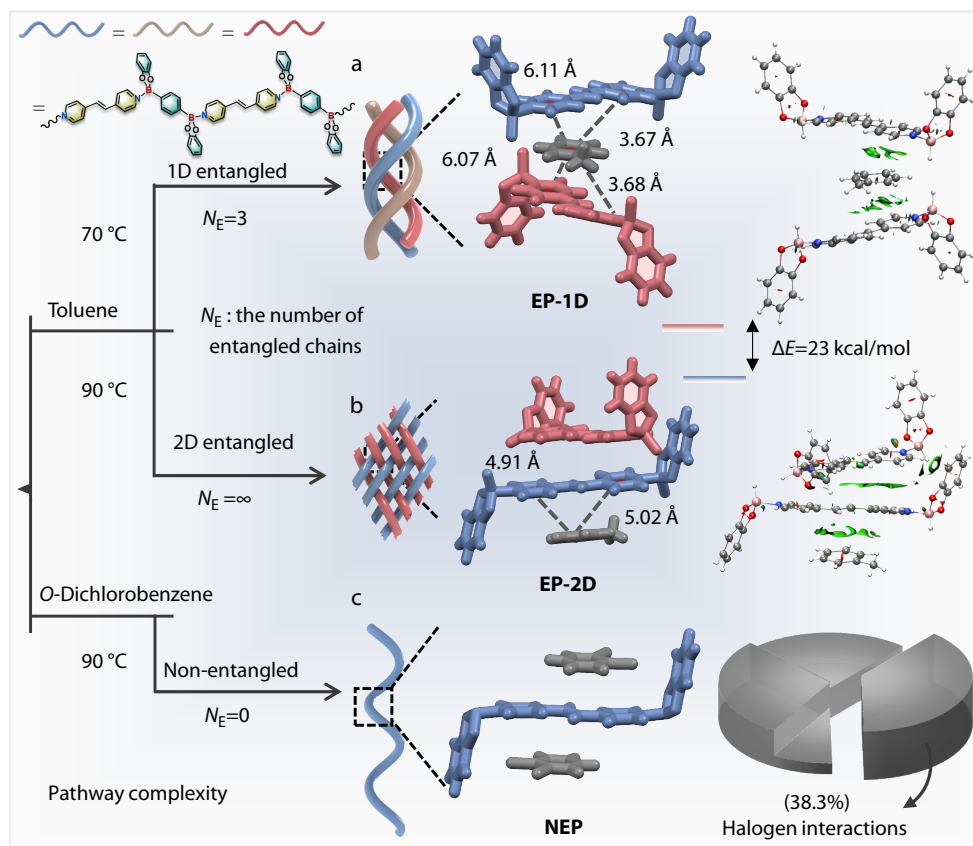


Fig. 2 (a) An entanglement node in the crystal structure of **EP-1D**. It is non-centrosymmetric, with pyridine-toluene distances of 6.11, 6.07, 3.68, and 3.67 Å. (b) An entanglement node in the crystal structure of **EP-2D**. The entanglement nodes in **EP-2D** exhibit higher stability than those in **EP-1D**. (c) A non-entangled part in the crystal structure of **NEP**. The polymer chains were fully solvated, primarily driven by halogen interactions.

ternative approach for evaluating their mechanical properties. Specifically, PeakForce quantitative nanomechanical (QNM) mapping of the three polymers was performed to thoroughly investigate the influence of the entanglement topologies on the mechanical response. The compressed axes were determined as a , b , and c axes for **NEP**, **EP-1D**, and **EP-2D**, respectively (Figs. S15–S17 in ESI). As shown in Figs. 3(a)–3(c), the average Derjaguin–Muller–Toporov (DMT) moduli of **NEP**, **EP-1D**, and **EP-2D** were 6.3, 2.3, and 2.1 GPa, respectively. Typical force versus separation curves are shown in Fig. S18 (in ESI). The results demonstrated enhanced elasticity by entangling polymer chains, and 2D entanglement further improved the elasticity compared to 1D entanglement. Furthermore, we calculated the Young's moduli in all

directions and simulated the crystal deformation of the three polymers under 15% uniaxial compression.^[41,42] First, the spatial dependence of Young's modulus was visualized by ELATE^[43] by calculating the second-order elastic constants (SOECs, Tables S4–S6 in ESI). As shown in Figs. 3(d) and 3(e), polymer entanglement leads to a more anisotropic 3D modulus pattern and a smaller average modulus value (E_V). Additionally, entangling the polymer chains into a 2D plane led to a 2D modulus distribution, as the warp-and-weft entanglement enabled a more uniform stress distribution within the 2D plane (Fig. 3f). Subsequently, structural deformations under a 15% compressive load were simulated using DFT calculations, to thoroughly investigate the entanglement effect from a kinematic perspective. The simulated structures under

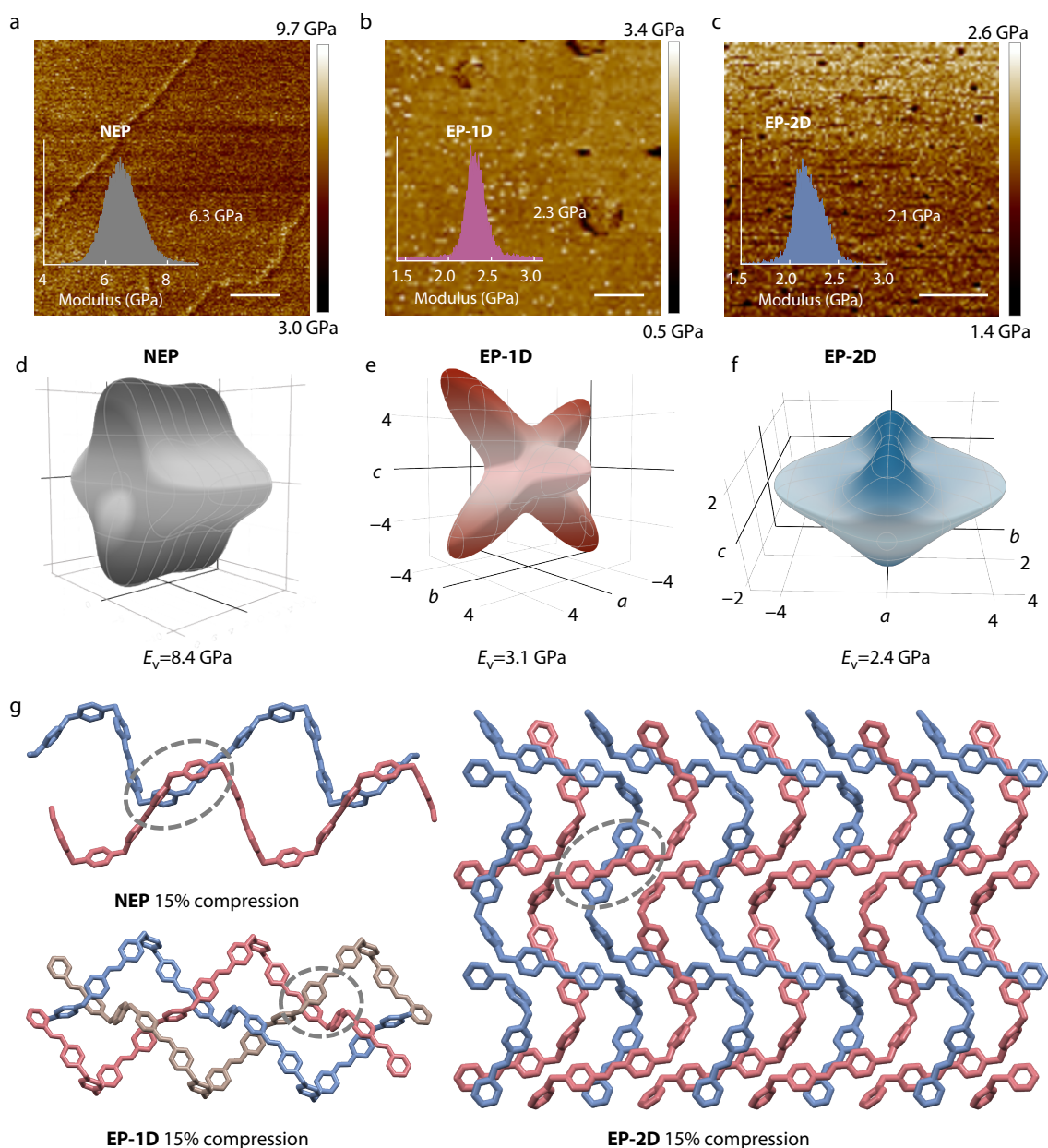


Fig. 3 Mappings of the DMT moduli of (a) **NEP**, (b) **EP-1D**, and (c) **EP-2D**. The scale bars are 0.5 μm . Calculated spatial-dependent Young's modulus plots for (d) **NEP**, (e) **EP-1D**, and (f) **EP-2D**. (g) Simulated deformed structures of the three polymers under 15% uniaxial compression.

15% compression are shown in Fig. 3(g) and Tables S7–S9 (in ESI), in comparison with the original pattern exhibited in Figs. 1(b)–1(d). Specifically, without entanglement, the polymer chains in **NEP** were found to be brought closer upon compression (highlighted by dashed boxes). Furthermore, the overall triple-helical topology of **EP-1D** remained, with distorted and uniaxially extended entanglement nodes. Subsequently, by increasing the number of entangled polymer chains to **EP-2D**, the topology structure remained almost unchanged under 15% compression. These results offer preliminary insights into the effects of entanglement patterns on structural stability.

Subsequently, to further investigate the molecular mechanisms of chain entanglement, the detailed deformation behaviors of unit cells and entanglement nodes were studied under progressive compression ranging from 0% to 15%. First, the variations in the crystallographic axes (Δa , Δb , and Δc) of the three polymers are depicted in Fig. 4(a), with the corresponding values at 15% compression summarized in Fig. 4(b). Notably, the compressed axes, Δa for **NEP**, Δb for **EP-1D**, and Δc for **EP-2D** were excluded as they were fixed at 15%. The results demonstrated that **NEP** exhibited maximum deformation (20.9%), followed by **EP-1D** (15.1%), and **EP-2D** (10.9%), confirming the superior structural stability of **EP-2D**. Second, the deformation characteristics of the entanglement

nodes and the associated energy changes were analyzed using DFT calculations (Figs. 4c–4f and Table S10 in ESI). For **NEP** (Fig. 4c), although the π - π stacking distances between *o*-dichlorobenzene molecules and polymer chains shortened under compression, the intermolecular interactions were attenuated due to the misalignment of the aromatic ring (Fig. 4f). Such weakened π - π interactions may account for the facile chain sliding observed in **NEP**. As for **EP-1D** (Fig. 4d), the sandwich-like entanglement nodes underwent significant structural distortion, leading to the progressive exclusion of the encapsulated solvent molecules with adaptive energy adjustments (Fig. 4f). This oscillatory energy profile reflects the dynamic equilibrium between solvent molecule expulsion and polymer chain reorganization, thereby imparting enhanced structural stability to **EP-1D**. In the case of **EP-2D** (Fig. 4e), the strong π - π interactions derived from the direct entanglement of polymer segments preserved nearly intact topological configurations under compression, with only a marginal displacement of solvent molecules. After compression, the entanglement nodes were strengthened (Fig. 4f) as the pyridine-pyridine distance decreased from 3.83 Å to 3.57 Å, endowing **EP-2D** with the optimal structural stability. Collectively, these findings elucidate how chain entanglement modulates the mechanical properties of polymers on the molecular scale.

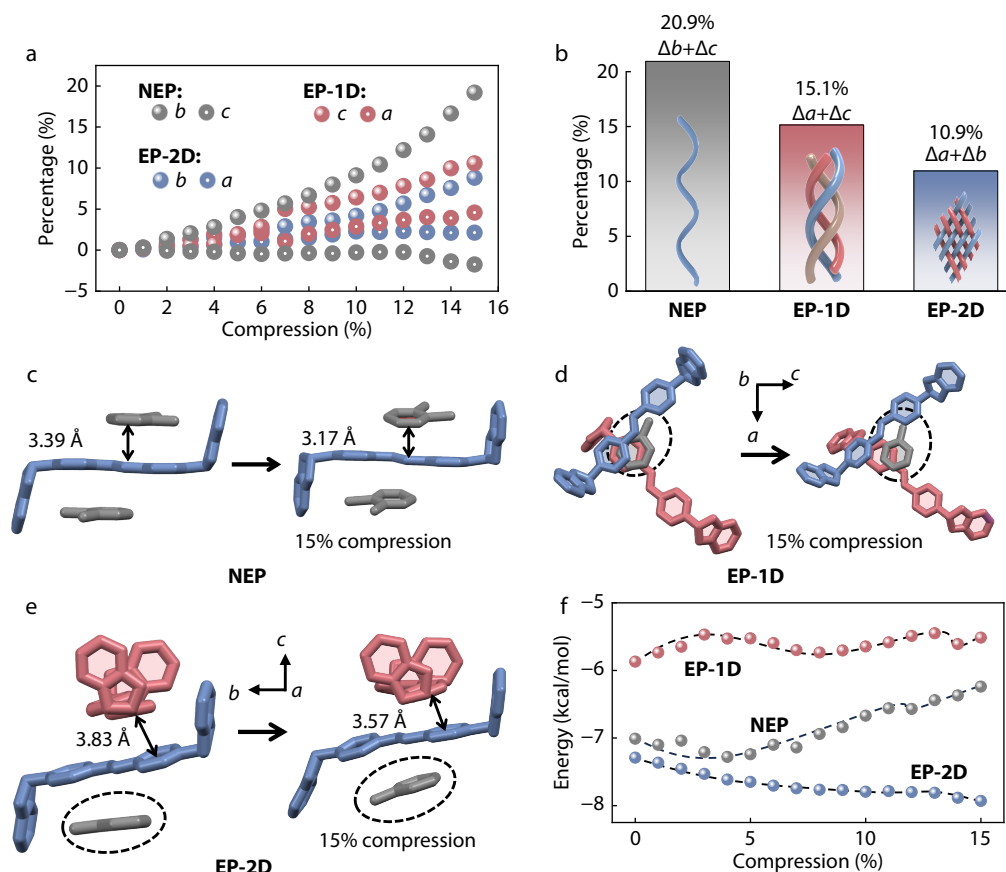


Fig. 4 (a) Variations in crystallographic axes of **NEP**, **EP-1D** and **EP-2D** under stepwise compression from 0% to 15%; (b) Summarized deformation rates of the three polymers under 15% compression. Detailed structures of (c) a non-entangled part of **NEP**, (d) an entanglement node of **EP-1D**, and (e) an entanglement node of **EP-2D** before compression and under 15% compression and their respective energy profiles (f) under stepwise

compression from 0% to 15%.

CONCLUSIONS

In summary, we have successfully constructed non-entangled, one-dimensional entangled, and two-dimensional entangled crystalline polymers by exploiting the bonding of dative B—N bonds and controlling their extended conformations, thereby providing a robust platform to investigate the role of entanglements in the mechanical behavior of polymers. By combining atomic force microscopy and density functional theory calculations, we have demonstrated that polymers with different entanglement topologies exhibit distinct structural stability and deformation mechanisms under applied stress. Specifically, compared to one-dimensional polymers containing a limited number of intertwined chains, two-dimensional entangled polymers, in which numerous chains are interwoven within a planar network, have shown superior resistance to deformation. Moreover, the modulation of entanglement point structures and their stress-responsive dynamics by solvents was investigated in this study, a factor that has largely been overlooked in previous studies of amorphous entangled polymers. Hence, this study provides a unique methodological approach and a novel perspective for investigating the influence of polymer entanglements on the ultimate material properties. By integrating structural control, advanced characterization techniques, and theoretical analysis, a new framework that is highly complementary to conventional dynamic polymer systems was established to elucidate the relationship between entanglement architecture and mechanical performance, thereby further advancing our fundamental understanding of the structure–property relationships in polymer materials. Furthermore, the investigation of entanglement–property relationships in crystalline polymers presented here represents only an initial step. It has the potential to inspire further studies using crystalline platforms to probe polymer properties or structure–property correlations that are challenging to access in conventional amorphous polymer systems, thereby offering valuable insights for future research.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-026-3862-8>.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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REFERENCES

- 1 Alemán, J.; Chadwick, A. V.; He, J.; Hess, M.; Horie, K.; Jones, R. G.; Kratochvil, P.; Meisel, I.; Mita, I.; Moad, G.; Penczek, S.; Stepto, R. F. T. Definitions of terms relating to the structure and processing of sols, gels, networks, and inorganic–organic hybrid materials. *Pure Appl. Chem.* **2007**, *79*, 1801.
- 2 Neumann, S. E.; Kwon, J.; Gropp, C.; Ma, L.; Giovine, R.; Ma, T.; Hanikel, N.; Wang, K.; Chen, T.; Jagani, S.; Ritchie, R. O.; Xu, T.; Yaghi, O. M. The propensity for covalent organic frameworks to template polymer entanglement. *Science* **2024**, *383*, 1337–1343.
- 3 Kumankuma-Sarpong, J.; Chang, C.; Hao, J.; Li, T.; Deng, X.; Han, C.; Li, B. Entanglement added to cross-linked chains enables tough gelatin-based hydrogel for Zn metal batteries. *Adv. Mater.* **2024**, *36*, 2403214.
- 4 Dhand, A. P.; Davidson, M. D.; Zlotnick, H. M.; Kolibaba, T. J.; Killgore, J. P.; Burdick, J. A. Additive manufacturing of highly entangled polymer networks. *Science* **2024**, *385*, 566–572.
- 5 Fu, L.; Li, L.; Bian, Q.; Xue, B.; Jin, J.; Li, J.; Cao, Y.; Jiang, Q.; Li, H. Cartilage-like protein hydrogels engineered via entanglement. *Nature* **2023**, *618*, 740–747.
- 6 Liang, C.; Dudko, V.; Khoruzhenko, O.; Hong, X.; Lv, Z.; Tunn, I.; Umer, M.; Timonen, J. V. I.; Linder, M. B.; Breu, J.; Ikkala, O.; Zhang, H. Stiff and self-healing hydrogels by polymer entanglements in co-planar nanoconfinement. *Nat. Mater.* **2025**, *24*, 599–606.
- 7 Zhong, D.; Wang, Z.; Xu, J.; Liu, J.; Xiao, R.; Qu, S.; Yang, W. A strategy for tough and fatigue-resistant hydrogels via loose cross-linking and dense dehydration-induced entanglements. *Nat. Commun.* **2024**, *15*, 5896.
- 8 Kim, J.; Zhang, G.; Shi, M.; Suo, Z. Fracture, fatigue, and friction of polymers in which entanglements greatly outnumber cross-links. *Science* **2021**, *374*, 212–216.
- 9 Guo, S.; Zhang, S.; Li, H.; Liu, S.; Koh, J.; Zhou, M.; Sun, Z.; Liu, Y.; Qu, H.; Yu, Z.; Zhang, Y.; Yang, L.; Chen, W.; He, C.; Lee, C.; Mao, D.; Ravi, S.; Lai, Y.; Tan, S. C. Precisely manipulating polymer chain interactions for multifunctional hydrogels. *Matter* **2025**, *8*, 101785.
- 10 Li, S.; He, X.; Zeng, Z.; Jiang, B.; Wu, Q.; Gong, L.; Li, Y.; Bae, J.; Wang, S.; Tang, L. Mechanically ductile, ionically conductive and low-temperature tolerant hydrogel enabled by high-concentration saline towards flexible strain sensor. *Nano energy* **2022**, *103*, 107789.
- 11 Nian, G.; Chen, Z.; Bao, X.; Tan, M. W. M.; Kutsovsky, Y.; Suo, Z. Natural rubber with high resistance to crack growth. *Nat. Sustain.* **2025**, *8*, 692.
- 12 Yang, J.; Bai, R.; Suo, Z. Topological adhesion of wet materials. *Adv. Mater.* **2018**, *30*, 1800671.
- 13 Hu, Y.; Teat, S.; Gong, W.; Zhou, Z.; Jin, Y.; Chen, H.; Wu, J.; Cui, Y.; Jiang, T.; Cheng, X.; Zhang, W. Single crystals of mechanically entwined helical covalent polymers. *Nat. Chem.* **2021**, *13*, 660–665.
- 14 Lázaro, I. A.; Chen, X.; Ding, M.; Eskandari, A.; Fairen-Jimenez, D.; Giménez-Marqués, M.; Gref, R.; Lin, W.; Luo, T.; Forgan, R. Metal-

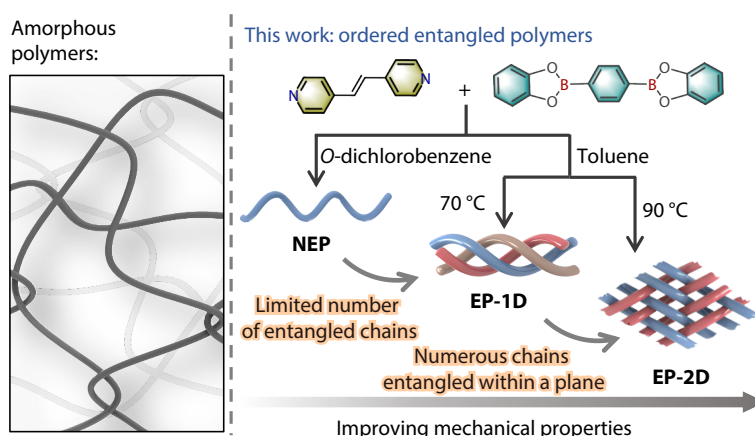
Graphical Abstract

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This study provides a unique approach and a novel perspective for investigating the influence of polymer entanglements on mechanical properties, inspiring further studies leveraging crystalline polymer platforms to probe polymer properties that are challenging to access in conventional amorphous polymer systems.



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- organic frameworks for biological applications. *Nat. Rev. Method. Prime.* **2024**, 4, 42.
- 15 Liu, Y.; Ma, Y.; Zhao, Y.; Sun, X.; Gándara, F.; Furukawa, H.; Liu, Z.; Zhu, H.; Zhu, C.; Suenaga, K.; Oleynikov, P.; Alshammari, A. S.; Zhang, X.; Terasaki, O.; Yaghi, O. M. Weaving of organic threads into a crystalline covalent organic framework. *Science* **2016**, 351, 365–369.
 - 16 Xie, X.; Zhang, X.; Xie, M.; Xiong, L.; Sun, H.; Lu, Y.; Mu, Q.; Rummeli, M.; Xu, J.; Li, S.; Zhong, J.; Deng, Z.; Ma, B.; Cheng, T.; Goddard, W.; Peng, Y. Au-activated N motifs in non-coherent cupric porphyrin metal organic frameworks for promoting and stabilizing ethylene production. *Nat. Commun.* **2022**, 13, 63.
 - 17 Li, H.; Eddaoudi, M.; O’Keeffe, M.; Yaghi, O. M. Design and synthesis of an exceptionally stable and highly porous metal-organic framework. *Nature* **1999**, 402, 276.
 - 18 Yaghi, O. M.; Li, G.; Li, H. Selective binding and removal of guests in a microporous metal-organic framework. *Nature* **1995**, 378, 703.
 - 19 Martí-Gastaldo, C.; Antypov, D.; Warren, J. E.; Briggs, M. E.; Chater, P. A.; Wiper, P. V.; Miller, G. J.; Khimyak, Y. Z.; Darling, G. R.; Berry, N. G.; Rosseinsky, M. J. Side-chain control of porosity closure in single- and multiple-peptide-based porous materials by cooperative folding. *Nat. Chem.* **2014**, 6, 343.
 - 20 Pathan, J. R.; Bhandary, S.; Sureshan, K. M. Two structurally different polymers from a single monomer. *J. Am. Chem. Soc.* **2023**, 145, 22633.
 - 21 Wu, T.; Huang, H.; Wang, J.; Luo, H.; Xu, J.; Ye, H. Polymer single crystal: from crystallization strategy to functionalized application. *Prog. Chem.* **2023**, 35, 1727.
 - 22 Balan, H.; Sureshan, K. M. Hierarchical single-crystal-to-single-crystal transformations of a monomer to a 1D-polymer and then to a 2D-polymer. *Nat. Commun.* **2024**, 15, 6638.
 - 23 Pathak, S.; Sureshan, K. M. A syndiotactic polymer via spontaneous exoselective single-crystal-to-single-crystal topochemical Diels-Alder cycloaddition reaction. *J. Am. Chem. Soc.* **2024**, 146, 30495.
 - 24 Zhang, J.; Wang, Z.; Suo, J.; Tuo, C.; Chen, F.; Chang, J.; Zheng, H.; Li, H.; Zhang, D.; Fang, Q.; Qiu, S. Morphological tuning of covalent organic framework single crystals. *J. Am. Chem. Soc.* **2024**, 146, 35090.
 - 25 Yang, Y.; Lin, E.; Wang, S.; Wang, T.; Wang, Z.; Zhang, Z. Single-crystal one-dimensional porous ladder covalent polymers. *J. Am. Chem. Soc.* **2024**, 146, 782.
 - 26 Khazeber, R.; Sureshan, K. M. Single-crystal-to-single-crystal translation of a helical supramolecular polymer to a helical covalent polymer. *Proc. Natl. Acad. Sci. U.S.A.* **2022**, 119, e2205320119.
 - 27 Liu, C. H.; Chen, L.; Zhang, H.; Li, Y.; Lin, H.; Li, L.; Wu, J.; Liu, C.; Ye, Z. M.; Xiang, S.; Chen, B.; Zhang, Z. A B—N framework based on 1D dative B—N polymers for exclusive recognition and separation of benzene from its azeotrope. *Chem* **2023**, 9, 3532–3543.
 - 28 Zhang, H.; Li, Y.; Chen, L.; Yang, Y.; Lin, H.; Xiang, S.; Chen, B.; Zhang, Z. A crystalline and stable microporous framework based

- on the dative B←N bonds. *Chem* **2023**, *9*, 242–252.
- 29 Wang, X.; Zhang, L.; Wang, X.; Cheng, T.; Xue, M.; Dong, Q.; Peng, Y.; Zhang, Q. Constructing covalent organic polymers through dative B–N bonds: synthesis, single crystal structures, and physical properties. *Adv. Funct. Mater.* **2024**, *35*, 2401362.
 - 30 Zhang, L.; Chen, Z.; Li, X. X.; Wang, X.; Gu, Q.; Wang, X.; Lee, C. S.; Lan, Y. Q.; Zhang, Q. A covalent organic nanoribbon: preparation, single crystal structure with chinese luban lock configuration, and photocatalytic behavior. *Angew. Chem. Int. Ed.* **2024**, *63*, e202411018.
 - 31 Xiao, X.; Xiao, D.; Sheng, G.; Shan, T.; Wang, J.; Miao, X.; Liu, Y.; Li, G.; Zhu, Y.; Sessler, J. L.; Huang, F. Formation of polyrotaxane crystals driven by dative boron–nitrogen bonds. *Sci. Adv.* **2023**, *9*, eadi1169.
 - 32 Sheng, X.; Wang, Z.; Sheng, G.; Zhu, C.; Xiao, D.; Shan, T.; Xiao, X.; Liu, M.; Li, G.; Zhu, Y.; Sessler, J. L.; Huang, F. Three-dimensional crystalline organic framework stabilized by molecular mortise-and-tenon jointing. *J. Am. Chem. Soc.* **2024**, *146*, 12547–12555.
 - 33 Shan, T.; Chen, L.; Xiao, D.; Xiao, X.; Wang, J.; Chen, X.; Guo, Q.-H.; Li, G.; Stoddart, J. F.; Huang, F. Adsorption of nonporous polymer crystals. *Angew. Chem. Int. Ed.* **2024**, *136*, e202317947.
 - 34 Vidal, F.; Gomezcoello, J.; Lalancette, R. A.; Jäkle, F. Lewis pairs as highly tunable dynamic cross-links in transient polymer networks. *J. Am. Chem. Soc.* **2019**, *141*, 15963–15971.
 - 35 Cromwell, O. R.; Chung, J.; Guan, Z. Malleable and self-healing covalent polymer networks through tunable dynamic boronic ester bonds. *J. Am. Chem. Soc.* **2015**, *137*, 6492–6495.
 - 36 Höpfl, H. The tetrahedral character of the boron atom newly defined—a useful tool to evaluate the N→B bond. *J. Organomet. Chem.* **1999**, *581*, 129–149.
 - 37 Sheepwash, E.; Krampl, V.; Scopelliti, R.; Sereda, O.; Neels, A.; Severin, K. Molecular networks based on dative boron–nitrogen bonds. *Angew. Chem. Int. Ed.* **2011**, *50*, 3034–3073.
 - 38 Xiao, D.; Jin, Z.; Sheng, G.; Chen, L.; Xiao, X.; Shan, T.; Wang, J.; Navik, R.; Xu, J.; Zhou, L.; Guo, Q.; Li, G.; Zhu, Y.; Stoddart, J. F.; Huang, F. Single crystals of purely organic free-standing two-dimensional woven polymer networks. *Nat. Chem.* **2024**, *16*, 1906–1914.
 - 39 Christinat, N.; Scopelliti, R.; Severin, K. Multicomponent assembly of boronic acid based macrocycles and cages. *Angew. Chem. Int. Ed.* **2008**, *47*, 1848–1852.
 - 40 Shan, T.; Chen, L.; Guo, Z.; Xiao, D.; Wang, M.; Xiao, X.; Li, G.; Huang, F. Designing high-mechanical-property organic polymeric crystals: insights from stress dispersion and energy dissipation strategies. *J. Am. Chem. Soc.* **2025**, *147*, 17477–17485.
 - 41 Thompson, A. J.; Chong, B. S. K.; Kenny, E. P.; Evans, J. D.; Powell, J. A.; Spackman, M. A.; McMurtrie, J. C.; Powell, B. J.; Clegg, J. K. Origins of elasticity in molecular materials. *Nat. Mater.* **2025**, *24*, 356–360.
 - 42 Meekel, E. G.; Partridge, P.; Paraoan, R. A. I.; Levinsky, J. J. B.; Slater, B.; Hobday, C. L.; Goodwin, A. L. Enhanced elastic stability of a topologically disordered crystalline metal–organic framework. *Nat. Mater.* **2024**, *23*, 1245–1251.
 - 43 Gaillac, R.; Pullumbi, P.; Coudert, F. X. ELATE: an open-source online application for analysis and visualization of elastic tensors. *J. Phys. Condens. Matter* **2016**, *28*, 275201.