

Bolstering the Mechanical Robustness of Supramolecular Polymer Network by Mechanical Bond

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 Electronic Supplementary Information

Abstract Supramolecular polymer networks (SPNs) are celebrated for their dynamic nature, yet they often exhibit inadequate mechanical properties. Thus far, the quest to bolster the mechanical resilience of SPNs while preserving their dynamic character presents a formidable challenge. Herein, we introduce [2]rotaxane into SPN to serve as another cross-link, which could effectively enhance the mechanical robustness of the polymer network without losing the dynamic properties. Compared with SPN, the dually cross-linked network (DPN) demonstrates superior breaking strength, Young's modulus, puncture force and toughness, underscoring its superior robustness. Furthermore, the cyclic tensile tests reveal that the energy dissipation capacity of DPN rivals, and in some cases surpasses, that of SPN, owing to the efficient energy dissipation pathway facilitated by [2]rotaxane. In addition, benefiting from stable topological structure of [2]rotaxane, DPN exhibits accelerated recovery from deformation, indicating superior elasticity compared to SPN. This strategy elevates the performance of SPNs across multiple metrics, presenting a promising avenue for the development of high-performance dynamic materials.

Keywords Rotaxane cross-links; Dually cross-linked network; Supramolecular polymer network; Host-guest recognition; Dynamic materials

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INTRODUCTION

Supramolecular polymer networks (SPNs) represent a class of macromolecules intricately interconnected by reversible supramolecular interactions,^[1–5] encompassing hydrogen bonding, metal coordination, hydrophobic interactions, and ionic attraction.^[6–9] Renowned for their remarkable dynamic attributes, including stimuli-responsive behaviors, self-healing capabilities, and inherent adaptabilities, SPNs hold promise for diverse applications.^[10–12] Yet, the presence of weak noncovalent bonds inherently poses challenges, manifesting in relatively diminished mechanical properties and stability, thus impeding their practical utility.^[13–15] Consequently, significant endeavors have been directed towards bolstering the mechanical robustness of SPNs.^[16–18] Among the myriad approaches explored thus far, the integration of covalent crosslinks into the SPN's network emerges as one of the most straightforward yet efficacious strategies, because chemical cross-link could guarantee superior strength, elasticity, and stability of the network.^[19–24] In our previous investigations, the incorporation of covalent

crosslink networks distinctly augmented the Young's modulus, strength, stability, and deformation recovery capacity of SPNs.^[25] Nonetheless, this enhancement came at the expense of reduced stretchability, toughness, and energy dissipation capacity, impacting the dynamic properties of the networks. We assume that if there is a cross-link mode that can enhance the robustness of SPNs while maintaining the high dynamicity of the network, SPNs with better performance could be developed.

A mechanical bond entails an entanglement in space between two or more component parts, rendering them inseparable without breaking or distorting the chemical bonds between atoms.^[26–30] The interlocked nature of these architectures confers significant conformational freedom and mobility to their components.^[31–35] Consequently, a mechanical bond's strength is akin to the weakest chemical bond within its structure, ensuring structural stability while maintaining considerable mechanical adaptivity due to its extensive conformational freedom.^[36–38] This unique attribute enables mechanical bonds to achieve a delicate balance between dynamicity and robustness.^[39–43] Exploiting this distinctive feature, mechanical bonds have been employed to cross-link polymer chains, offering notable property advantages.^[44–46] For instance, Ito and colleagues harnessed the rotaxane structure to develop slide-ring materials (SRMs), where the motion of mechanical bonds redistributes stress within the network,

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mitigating stress concentration.^[47] Similarly, Takata *et al.* devised a strategy to strengthen and toughen polymer networks by employing [2]rotaxane crosslinkers, with control over the mobile distance and mobility of the constituent components.^[46,48] Building upon these insights, we posit that the integration of mechanically interlocked cross-links into SPNs could enhance their robustness while preserving the network's high dynamicity. However, the synergistic utilization of supramolecular and mechanically interlocked cross-links to bolster the mechanical properties of SPNs remains rarely explored.

Herein, we introduce the [2]rotaxane into supramolecular polymer network (DPN) with supramolecular and mechanically interlocked cross-links, which exhibit enhanced robustness yet comparable high dynamic properties compared to SPN. The introduction of [2]rotaxane cross-links is based on a thiol-ene click reaction utilizing a thiol-functionalized [2]rotaxane. In tensile tests, DPN exhibits reduced elongation (330% versus 496%) compared to SPN, but demonstrates enhanced Young's modulus (15.8 MPa versus 2.1 MPa), toughness (14.5 MJ/m³ versus 11.4 MJ/m³), and strength (8.2 MPa versus 3.7 MPa). Meanwhile, DPN exhibits a higher resistance to puncture

forces (1.8 N versus 0.3 N) than SPN. In cyclic tensile tests, DPN shows higher energy dissipation ability than SPN, because rotaxane cross-links not only retain the same host-guest recognition interaction as supramolecular cross-links but also possess an additional sliding mechanism, providing a consecutive energy dissipation pathway. Furthermore, DPN is able to recover more rapidly after loading and unloading cycle in the recovery experiments, which benefits from the unique stability of [2]rotaxane cross-links enabled by the interlocked topology structure.

EXPERIMENTAL

The experimental sections are detailed in the electronic supplementary information (ESI).

RESULTS AND DISCUSSION

Design, Synthesis and Structural Characterization

To preserve comparable levels of binding strength in the host-guest recognition exhibited by supramolecular and rotaxane cross-linkers, the benzo-21-crown-7 (B21C7) has been uniformly employed as the crown ether host across both systems. Poly-

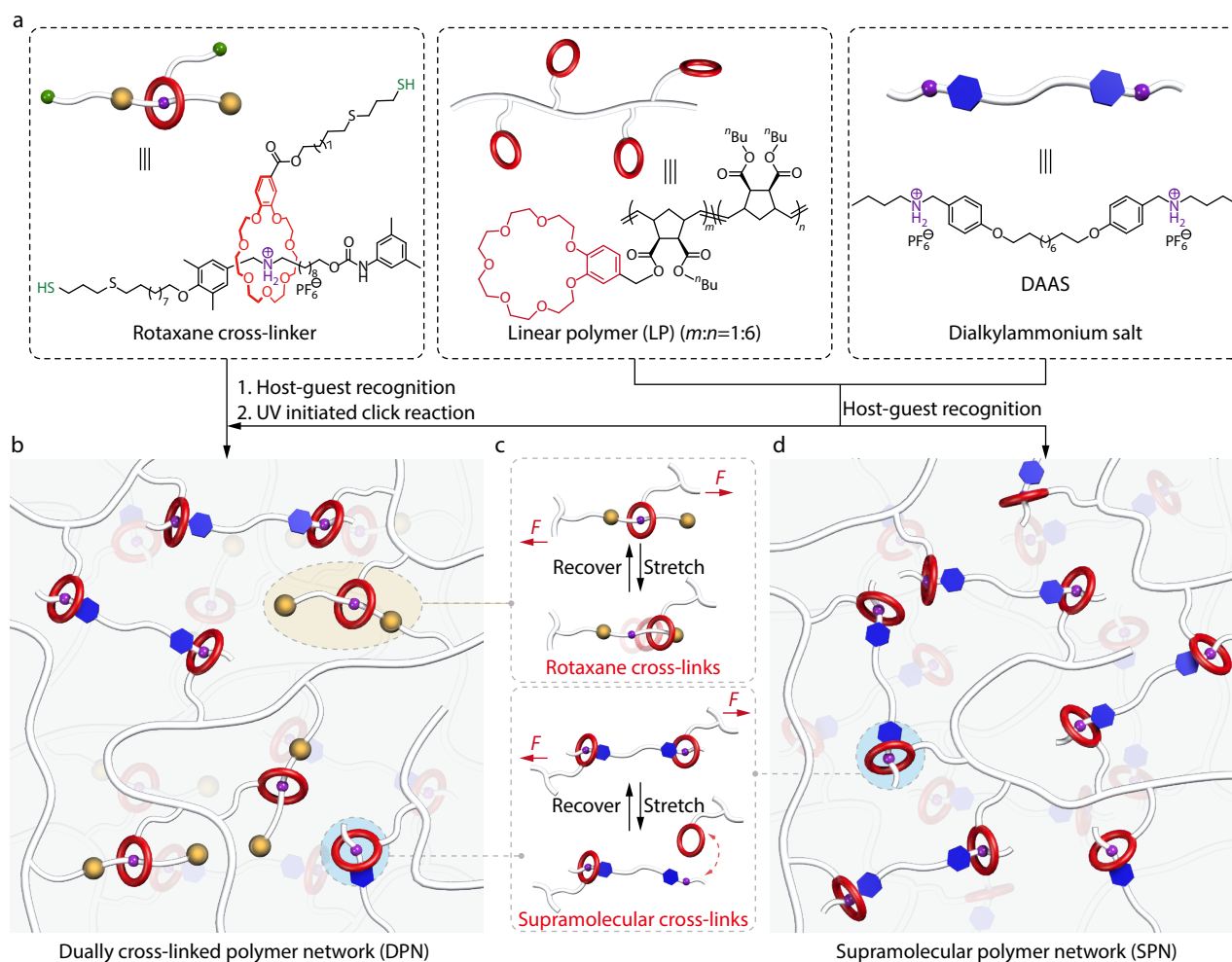


Fig. 1 (a) Chemical structures and corresponding schematic representations of rotaxane cross-linker, liner polymer and dialkylammonium salt; Schematic illustration of the network structures of (b) DPN and (d) SPN; (c) Different behaviors of two kinds of cross-links upon external force.

norbornene was chosen as the main chain for construction of networks due to its ease of modification and the presence of C=C sites along the backbone that could participate in cross-linking reactions. The linear polymer (LP) ($M_n=77$ kDa) was synthesized via ring-opening metathesis polymerization (ROMP) between the B21C7 decorated and the norbornenyl *exo*-di-*n*-butyl ester with a feed ratio of 1:6, initiating by the third-generation Grubbs catalyst (Fig. 1a). As for the preparation of the networks, firstly, LP and the dialkylammonium salt (DAAS) were dissolved in a mixed solvent (DMF/CH₂Cl₂=1:1), which was then evaporated under vacuum conditions at high temperature (80 °C). During this process, the crown ether in LP interacted with the secondary ammonium salt recognition sites on DAAS, leading to the formation of the fully cross-linked SPN (Fig. 1d). Subsequently, half of the DAAS was substituted with rotaxane cross-linkers to prepare the dually cross-linked network with the same cross-linking density. Similarly, the supramolecular cross-linking process was initially accomplished by dissolving DAAS, LP, rotaxane cross-linker, and 2,2-dimethoxy-2-phenylacetophenone (DMPA) in a mixed solvent (DMF:CH₂Cl₂=1:1), followed by evaporating the solvent under the same conditions. The prefabricated film was exposed to UV light (365 nm), enabling the successful construction of DPN in the bulk state through the thiol-ene click reaction between the C=C bonds of the LP backbone and the thiols of the [2]rotaxane (Fig. 1b).

With the two materials in hand, we proceeded to conduct detailed structural characterizations. Initially, the two network was characterized through the Fourier transform infrared spectroscopy (FTIR). In the spectra of DPN and [2]rotaxane, the characteristic bands corresponding to C—S stretching vibration at 700–660 cm⁻¹, which was not observed in the

spectra of LP and SPN, proving the success of the thiol-ene click reaction. Meanwhile, the stretching vibration bands of P—F at 842 cm⁻¹ could be found in the spectra of [2]rotaxane, DPN and SPN, indicating the presence of the rotaxane or supramolecular cross-links. To further demonstrate the formation of distinct cross-linked networks, swelling tests were conducted in acetonitrile (Fig. 2b). For DPN, the network exhibited a swelling behavior similar to covalent cross-links, with the swelling ratio gradually increasing until reaching equilibrium (Fig. 2c). On the contrary, SPN underwent rapid swelling followed by gradual dissolution, and these results were consistent with their different cross-linked structures.

Thermal Properties of the DPN and the SPN

The fundamental thermal properties of the DPN and SPN were evaluated using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA curves demonstrated the good thermal stability of the polymer materials, as evidenced by the decomposition temperatures (5% weight loss) of both samples were higher than 260 °C (Fig. S4 in ESI). In addition, the DSC curves showed the glass transition temperature (T_g) values of -1.2 and 4.2 °C for SPN and DPN, respectively (Fig. 2d). The structural similarity of these two cross-linked networks was manifested in their identical host-guest structures and recognition interaction, resulting in the small difference in T_g between these two materials. However, rotaxane cross-linkers were connected to polymer chains through the thiol-ene click reaction, introducing rigid, permanent cross-linking points into the network. This kind of modification influenced the motility of the entire network of DPN, which could be reflected in an increase in the value of T_g .

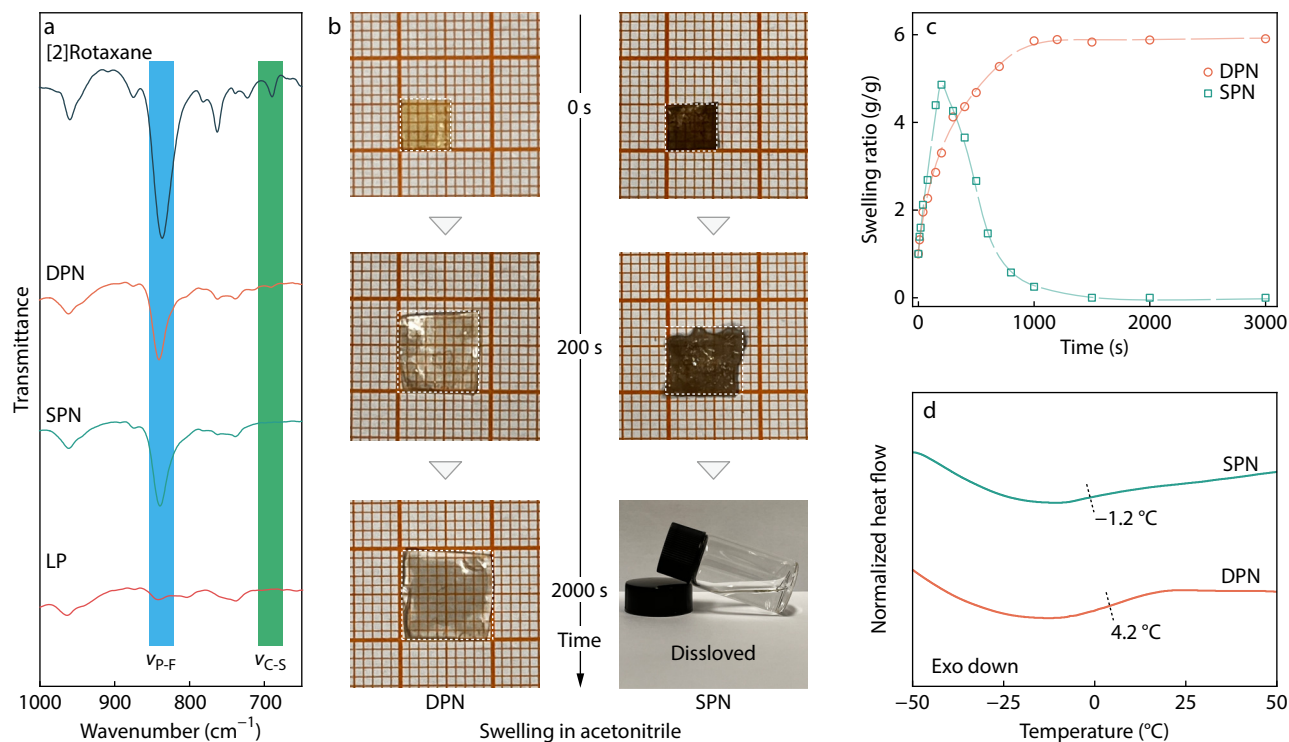


Fig. 2 (a) FTIR spectra of [2]rotaxane, DPN, SPN and LP; (b) Pictures showing the swelling processes of the DPN and SPN; (c) Swelling ratio curves of DPN and SPN in acetonitrile; (d) DSC curves of DPN and SPN measured by the second heating scan with a rate of 20 °C/min.

Mechanical Properties of the DPN and the SPN

To explore the impact of rotaxane and supramolecular cross-links on polymer networks, comprehensive mechanical assessments were conducted using tensile and puncture tests. The stress-strain curves for the DPN and SPN were depicted in Fig. 3(a), clearly demonstrating variations in strength and elongation that arose from the differing cross-linking modes. Compared to SPN, which was exclusively composed of supramolec-

ular cross-links, DPN exhibited higher breaking strength (8.2 MPa versus 3.7 MPa) but reduced tensile strain (330% versus 496%). Additionally, DPN displayed a higher Young's modulus (15.8 MPa versus 2.1 MPa) and greater toughness (14.5 MJ/m³ versus 11.4 MJ/m³), further differentiating its mechanical properties from those of SPN. Similar results could also be observed in puncture resistance experiments (Figs. 3c and 3d). Under identical testing conditions, DPN exhibited superior puncture

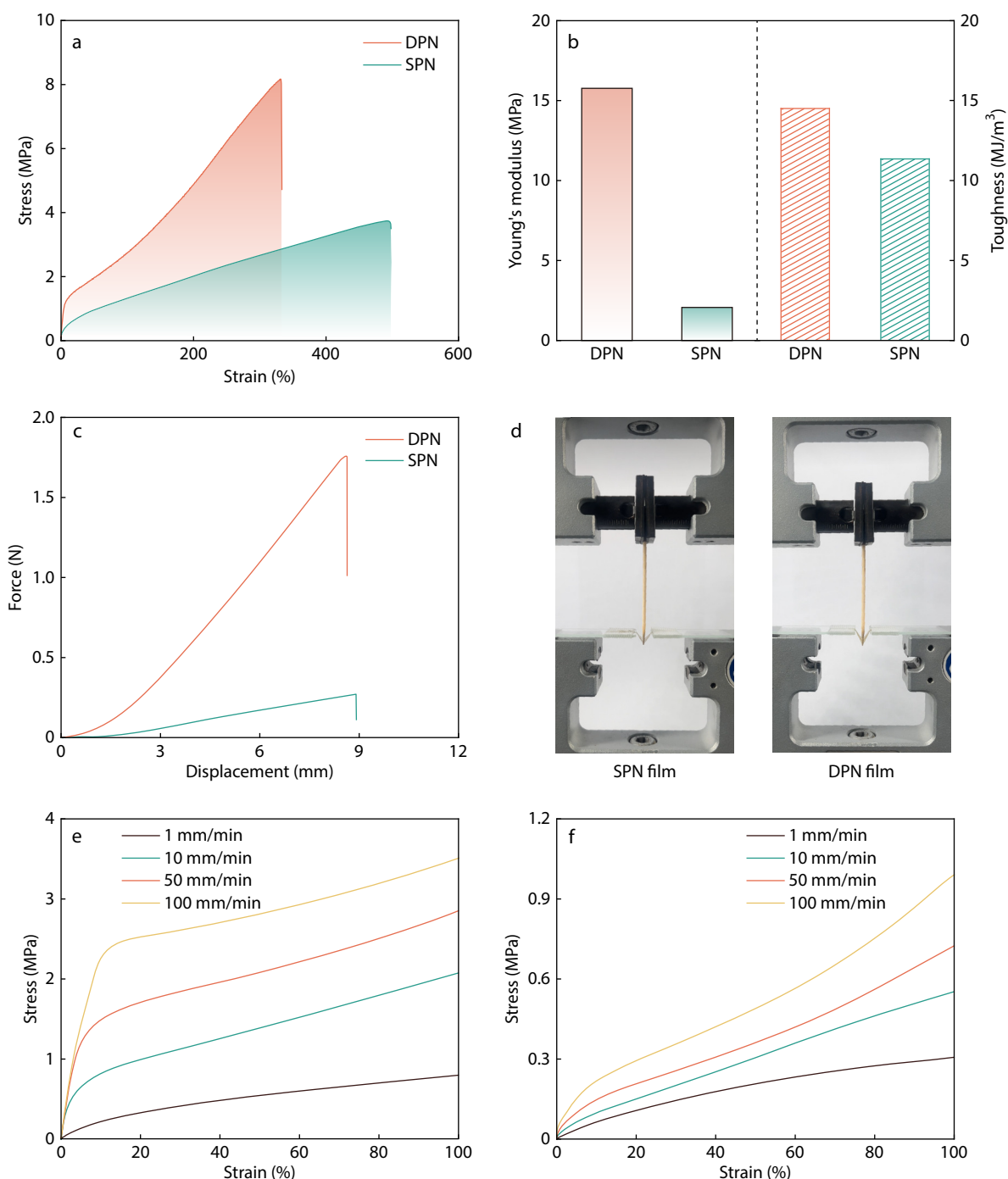


Fig. 3 (a) Stress-strain curves of DPN and SPN recorded with a deformation rate of 100 mm/min; (b) Young's modulus and toughness of DPN and SPN calculated from their stress-strain curves; (c) Puncture force-displacement curves of DPN and SPN; (d) Photographs of SPN and DPN films during the puncture resistance test; Tensile test curves of (e) DPN and (f) SPN with different deformation rates from 1 mm/min to 100 mm/min.

resistance compared to SPN, demonstrating both a similar displacement (8.6 mm versus 8.9 mm) and a higher puncture force (1.8 N versus 0.3 N). The differences in mechanical properties between the materials undoubtedly stem from the variations in their cross-linking methods. Under external forces, the dissociation of host-guest recognition interactions within SPN materials reduced the cross-linking density of the polymer network, resulting in the low strength. In contrast, the introduction of rotaxane cross-linkers endowed DPN with the stable structure and unique intramolecular sliding motion, which maintained their ability to dissipate energy but strengthened the network at the same time.

Additionally, tensile tests were then conducted at varying rates to investigate the effects of supramolecular interaction in these materials. The resulting stress-strain curves at deformation rates of 1, 10, 50 and 100 mm/min are shown in Figs. 3(e) and 3(f). It was evident that both SPN and DPN exhibited the rate-dependent characteristic, attributable to the presence of host-guest recognition within their structures. In both polymers, the dissociation of dynamic bonds required a certain amount of duration. If the stretching rate was too fast, the network deformed elastically before the bonds could dissociate, resulting in a higher Young's modulus (Fig. S5 in ESI).

Energy Dissipation and Recovery Properties of DPN and SPN

Supramolecular interaction and mechanically interlocked structure could introduce unique dynamic mechanisms to materials, which has been extensively documented in numerous studies.^[49–51] In this section, cyclic tensile tests and recovery experiments were conducted on DPN and SPN respectively to investigate the differences in the dynamic characteristics attributable to the two cross-linking modes. Evident hysteresis areas could be observed between loading and unloading curves

of both DPN and SPN (Figs. 4a and 4b), indicating the presence of the capacity of energy dissipation. Additionally, as the maximum strains escalated from 50% to 300%, the hysteresis area progressively enlarged while maintaining a similar damping ratio (Figs. 4c and 4d). Upon comparing the damping capacity values between these two materials which reflect the ratio of energy dissipation to the incoming energy, it was evident that DPN exhibited superior performance across both evaluated domains. This observation demonstrated that the dual dissipation mechanism, arising from both host-guest recognition and rotaxane sliding during the loading and unloading of DPN, provided a more significant energy dissipation capability than that achieved through single host-guest interaction alone.

Subsequently, the recovery properties of the two materials were assessed through tensile tests conducted at room temperature. As depicted in Figs. 4(e) and 4(f), DPN and SPN were subjected to loading and unloading cycles at a strain of 200%, following varying rest intervals. At this stress level, it was guaranteed that the samples would not break and the dynamic interactions in the systems could operate effectively. When DPN was stretched again immediately without undergoing a recovery interval, it exhibited a residual strain of approximately 50% and reduced strength, indicating that the network did not recover quickly from deformation. After a 10-min recovery interval, recover ratio rebounded to 85% (Fig. S6 in ESI), with full restoration of tensile strength. The recovery test results for SPN material displayed a similar trend, showing a residual strain of about 25% after the cycle tensile without any rest period. However, SPN must take a longer time to regain its performance. After 10-min recovery interval, the recovery ratio of SPN only reached 74%, and it required 30 min to restore most of its performance. The results of the recovery experiments highlighted differences in the dynamic prop-

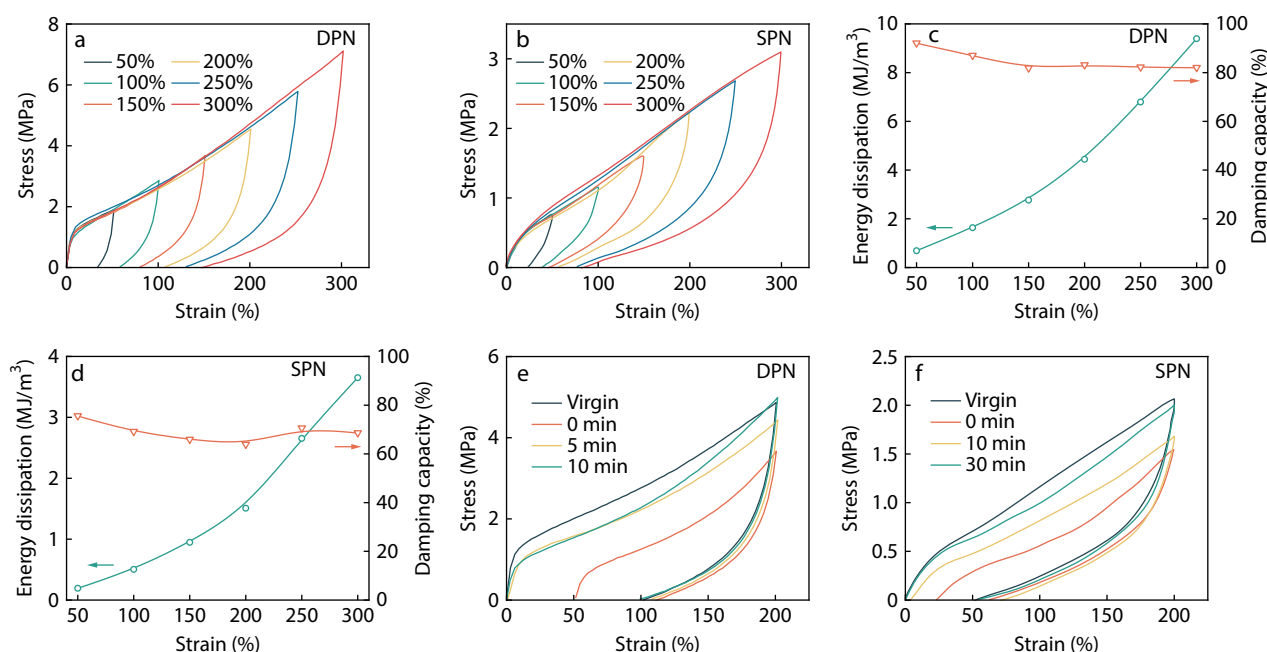


Fig. 4 Cycle tensile test curves of (a) DPN and (b) SPN; Energy dissipation and damping capacity for each circle of (c) DPN and (d) SPN; (e) DPN loaded at a strain of 200% with rest intervals at 0, 5 and 10 min; (f) SPN loaded at a strain of 200% with rest intervals at 0, 10 and 30 min. The tests were conducted with a deformation rate of 100 mm/min at room temperature.

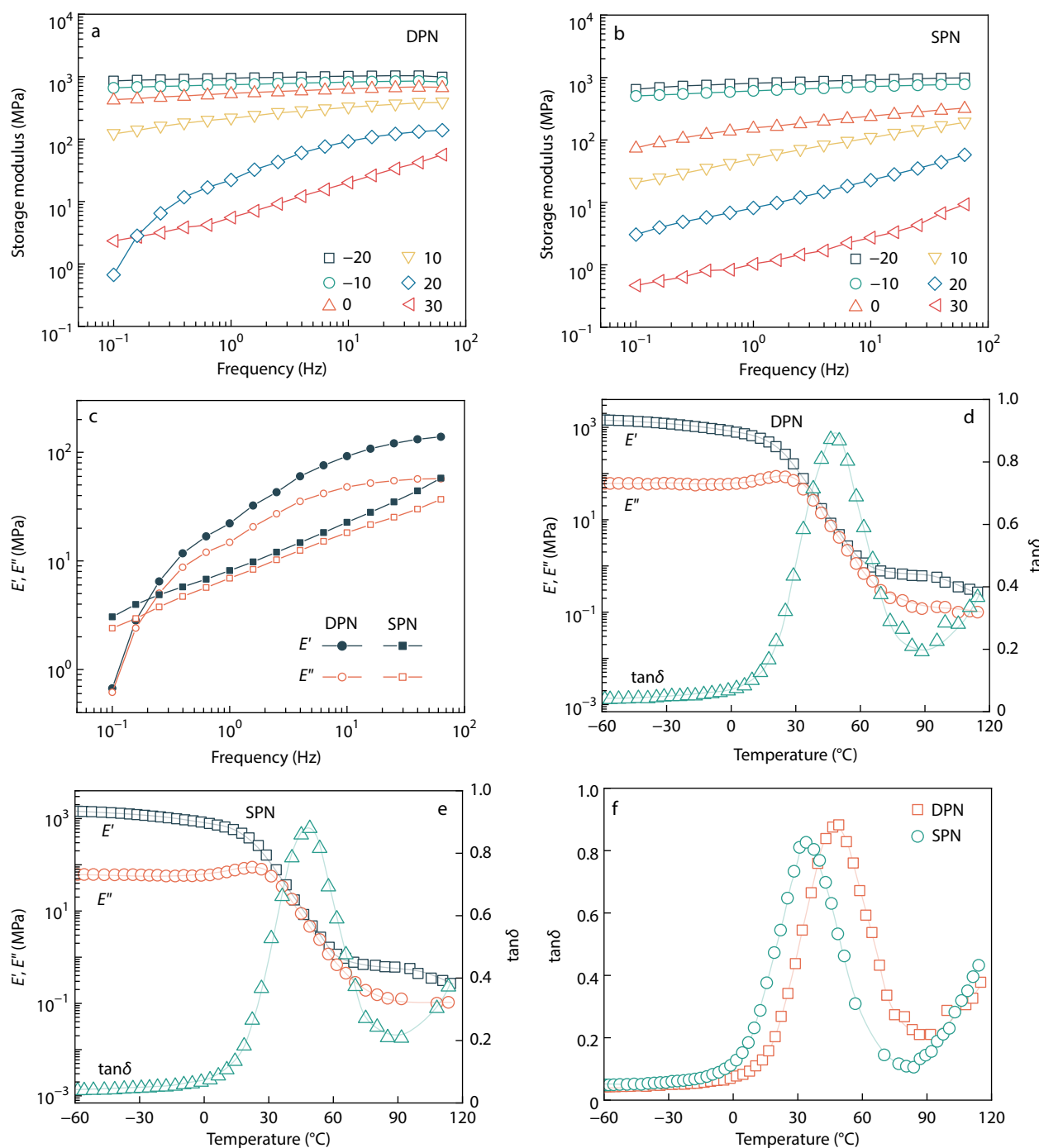


Fig. 5 Storage modulus of (a) DPN and (b) SPN from -20 °C to 30 °C measured by the frequency sweep; (c) Storage modulus and loss modulus of DPN and SPN at 20 °C; Storage modulus, loss modulus and dissipation factor $\tan\delta$ curves of (d) DPN and (e) SPN measured by the temperature ramp; (f) Comparison of $\tan\delta$ values of DPN and SPN.

erties of the materials attributed to the two kinds of cross-linkers, which stem from their distinct chemical structural. Although supramolecular cross-links could facilitate energy dissipation and recovery through the dynamic process of host-guest dissociation and recognition, these cross-linking structures might be disrupted under external forces. This destruction of this non-covalent interaction necessitated a period of re-recognition, leading to a prolonged recovery time. However,

the stopper groups in the rotaxane cross-linkers prevented the crown ether ring from sliding out, so that mechanically interlocked structure ensured the integrity and stability of the system. During the recovery process, the crown ether ring in the mechanical bond could slide along the axis and approach to re-recognition, which drove the movement of the network and thus facilitated the reconstruction of supramolecular cross-links, thereby hastening the material's

recovery process.

Viscoelastic Behaviors of the DPN and the SPN

To investigate the differences of viscoelastic behaviors resulting from the two cross-linking modes, the storage modulus (E'), loss modulus (E'') and loss factor ($\tan\delta$) of the two materials were measured under various conditions by dynamic mechanical analysis (DMA) with frequency sweep and temperature ramp modes. As shown in Figs. 5(a) and 5(b), as the temperature rises, there is a progressive decline in the values of E' observed for both materials. However, the E' of DPN always remained higher than that of SPN, suggesting that the dual cross-linking strategy employed in DPN confers enhanced elasticity. Additionally, it was notable that the modulus values of SPN began a rapid decline at 0 °C, whereas the transition for DPN occurred at 10 °C, indicating that the supramolecular cross-linked network in SPN was more susceptible to segmental motion. By analyzing the E' and E'' of the two materials at 20 °C (Fig. 5c), it was evident that DPN not only adhered to the aforementioned lows but also exhibited a distinct transition from the glassy state to the rubbery state.

Subsequently, temperature ramp tests of DPN and SPN were conducted with the results shown in Figs. 5(d) and 5(e). When the temperature was ramped up from –60 °C to 120 °C, both the E' and E'' decreased, and the values of E' were always larger than E'' over the whole temperature range, showing good thermomechanical stability of two networks. Analyzing the trend of the curves for the two materials, it was observed that following the transition peaks (about 35 °C for SPN, 45 °C for DPN) in the $\tan\delta$, both materials entered the plateau region at approximately 60 °C. Upon comparing the $\tan\delta$ curves of the two materials, the peak temperature for DPN was higher than that for SPN, aligning with the T_g trend presented in Fig. 2(d). Furthermore, the maximum $\tan\delta$ value of DPN was 0.89, which was slightly higher than SPN, observed at 0.83. The temperature range over which the $\tan\delta$ value of DPN exceeded 0.3 span approximately 50 °C, in contrast to SPN, where this range was about 43 °C. These results suggested that DPN, with its dual dissipation mechanism, exhibited a stronger energy dissipation and superior damping capacity compared to SPN's single energy dissipation mechanism.

CONCLUSIONS

In summary, based on the supramolecular cross-linked network, we constructed a novel dually cross-linked network DPN by introducing rotaxane cross-linker. The cross-linking density of SPN and DPN had been designed to be consistent through careful adjustment of the feed ratio and utilization of efficient thiol-ene click reaction. Tensile tests were conducted to evaluate and compare the mechanical properties of the two networks, providing insights into the performance of the dual cross-linking modes. Although there was a reduction in elongation (330% versus 496%), owing to the formation of permanent cross-linking points, the introduction of rotaxane cross-linkers not only significantly enhanced the Young's modulus (15.8 MPa versus 2.1 MPa) and strength (8.2 MPa versus 3.7 MPa), but also imparted higher toughness (14.5 MJ/m³ versus 11.4 MJ/m³) through the intramolecular rotaxane sliding mechanism. Furthermore, this additional energy dissipation pathway endowed the mate-

rial with better damping capacity, overcoming the inherent disadvantages of traditional covalent cross-linking. After stretching, the presence of the stopper in the rotaxane cross-linker could ensure the stability of the network, facilitating the recovery process of the material, which enabled DPN to demonstrated higher recovery ratio in the same time (0.85 versus 0.74, after 10-min recovery). Over all, this strategy not only bolstered the structural stability of supramolecular polymers and strengthened the cross-linked network, but also introduced additional pathways for energy dissipation to enhance the toughness. We believed this combination of mechanical and non-covalent bond was expected to be applied in various modification design where mechanical robustness was essential and contribute to the enhancement of mechanical properties.

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/s10118-024-3168-7>.

Data Availability Statement

The related data (DOI: 10.57760/sciencedb.j00189.00008) for this paper is available in the (Bolstering the Mechanical Robustness of Supramolecular Polymer Network by Mechanical Bond) database (<https://www.scidb.cn/c/cjps>).

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