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Perspective

Mechanochemistry for On-Demand Polymer Network Materials

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ABSTRACT: Contemporary polymer network materials, such as hydrogels and elastomers, require not only enhanced mechanical properties but also adaptability during or after use. Polymer mechanochemistry, which utilizes mechanical force to induce chemical reactions within polymers, has shown great potential in meeting these demands. This Perspective will explore how mechanophores, when integrated into polymer networks, can regulate microscale fracture pathways, either strengthening or weakening the materials. Additionally, it will examine how force-induced bond scission can trigger additional chemical reactions to adaptively adjust the polymer structures for on-demand functions. These force-activated chemical reactions could lead to strategies for strengthening, reshaping, and patterning materials through polymer growth, or, conversely, result in extensive bond scission and material degradation. The Perspective will also highlight the great potential of tough double network hydrogels as mechanochemical materials that can use mechanical energy to drive chemical reactions in an efficient and controllable manner. This opens up new possibilities for developing force-triggered "living materials" similar to biological systems.

1. INTRODUCTION

The broad application of polymer network materials, including gels and elastomers, across various fields requires on-demand design of their structure and mechanical properties. These demands encompass improvements in stiffness, stretchability, and toughness, as well as the development of materials capable of adapting their structure and performance in response to stimulus, for instance including self-healing upon damage,[1−3] tunable elastic/plastic deformation,[4−6] and the ability to be strengthened[7−18] or degraded[19−28] as needed during or after use. The mechanical behavior of polymer network materials is determined by their chemical composition and polymeric structures, key factors include chain length, cross-linking density, interactions between chains, network topology, and higher-order structures like phase separation and crystallization.[29] To achieve the desired properties, extensive efforts have been made to manipulate these factors, with polymer mechanochemistry emerging as a promising approach.

The concept of polymer mechanochemistry involves leveraging force to induce chemical reactions within polymer materials, achieving mechanoresponsive functions such as self-reporting of stress, strain, or damage through color changes[30−33] and force-responsive small molecule release.[20−23,34−42] Various aspects of polymer mechanochemistry, from mechanophore design to their practical application, have been extensively reviewed in the literature.[43−49] Recently, much attention has been focused on how mechanochemistry can modulate the structure and mechanical properties of bulk polymer network materials (Figure 1).

To achieve this, researchers have employed mechanoresponsive units, known as mechanophores, to alter the mechanical response of individual polymer chains to external forces, thereby largely changing the network fracture pathways in bulk materials.[50−55] As a result, crack propagation can be either delayed or accelerated, allowing for direct and precise regulation of the material's mechanical properties.

Furthermore, researchers utilize mechanical stimuli to adaptively modify polymer network structures and mechanical properties. Compared to chemical, thermal, or light stimuli, mechanical force provides a readily applied and versatile means of activation. When force is applied, it induces bond scission in the polymer network to generate new reactive sites, such as radicals[11,56−62] and acids,[19−22] which trigger further reactions to adjust the network structure. This process can facilitate new bond formation to generate additional cross-linking points and incorporate external substances into the materials, thereby enhancing their mass, strength and functionality.[7−10,18] Conversely, it can also accelerate degradation by inducing more bond cleavage.[19−24] With various mechanophores and chemical reactions supporting these processes, polymer mechanochemistry holds significant potential for achieving mechanically adaptive mechanical properties.

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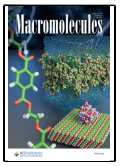

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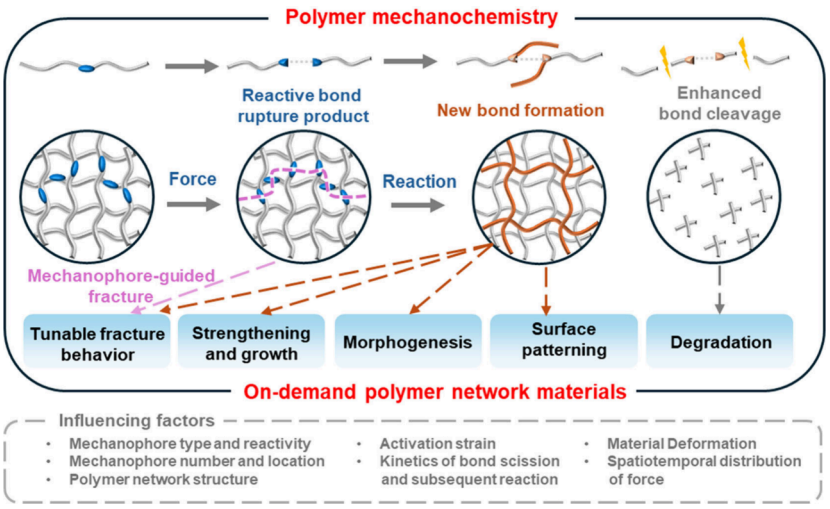

Figure 1. Routes utilizing polymer mechanochemistry to design on-demand polymer network materials and the crucial factors inside. Mechanophores are incorporated into the polymer network to regulate the microscale fracture pathways and resultant macroscale fracture behavior. More importantly, force-induced bond scission can trigger additional chemical reactions to adaptively adjust the polymer structures for on-demand functions.

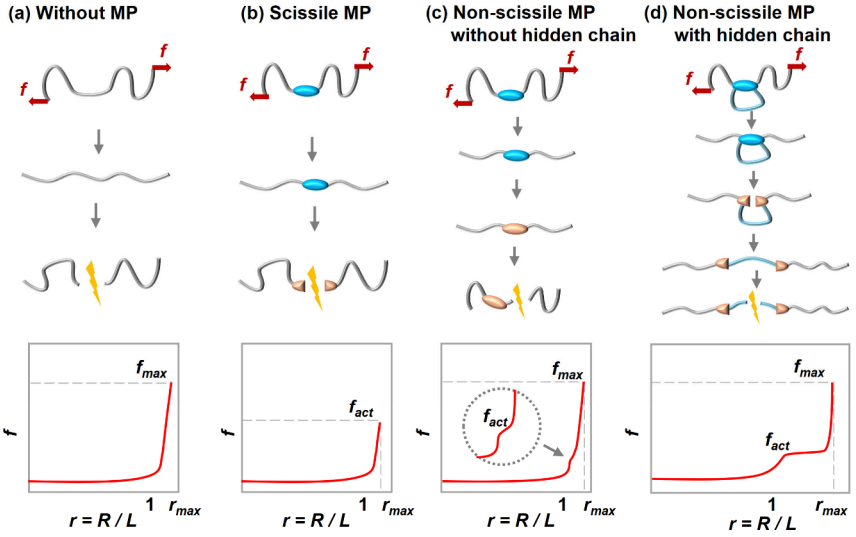

Figure 2. Illustration of various types of mechanophores (MP) and the effect of their incorporation on the tensile force (f) − normalized displacement ($r = R/L$, the ratio of end-to-end length R to contour length L) of a single polymer chain. f_{act} is the activation force of the mechanophore. r_{max} and f_{max} are the maximum normalized displacement and maximum tensile force of a single polymer chain, respectively.

In this Perspective, we summarize recent progress in leveraging mechanochemistry for designing mechanical properties of polymer networks. We first review how different mechanophores with various activation modes affect the stretching behavior of individual chains and, consequently, alter microscale network fracture pathways and macroscopic mechanical properties in different bulk polymer network materials. We then discuss how force-induced bond rupture products can trigger different reactions to adaptively modify the polymer structure and mechanical properties, achieving various functions in response to force. We focus on bulk materials subjected to macroscale forces such as stretching, compression, and shearing, with particular emphasis on force-triggered polymer growth in tough double network hydrogels. The influencing factors such as kinetics of bond scission and subsequent chemical reactions, deformation effects, and force spatiotemporal distribution are discussed in detail. We also discuss the force-triggered polymer degradation via enhanced bond cleavage. Finally, we discuss the challenges and opportunities of polymer mechanochemistry strategies for developing on-demand polymer network materials.

2. MECHANOPHORE-GUIDED NETWORK FRACTURE PATHWAY

The original and still primary intention behind incorporating mechanophores in polymeric materials is to enable self-reporting of strain, stress, or damage experienced by the polymer.[63] For this purpose, the incorporation of mechanophores should not alter the polymer's structure or mechanical properties, and their activation should accurately reflect the internal structural changes within the research materials. However, the concept has since evolved; there is now also an interest in using mechanophores to control bond scission sites within the polymer network to achieve desired mechanical properties. Currently, various mechanophores have been developed, each with different activation modes (scissile or

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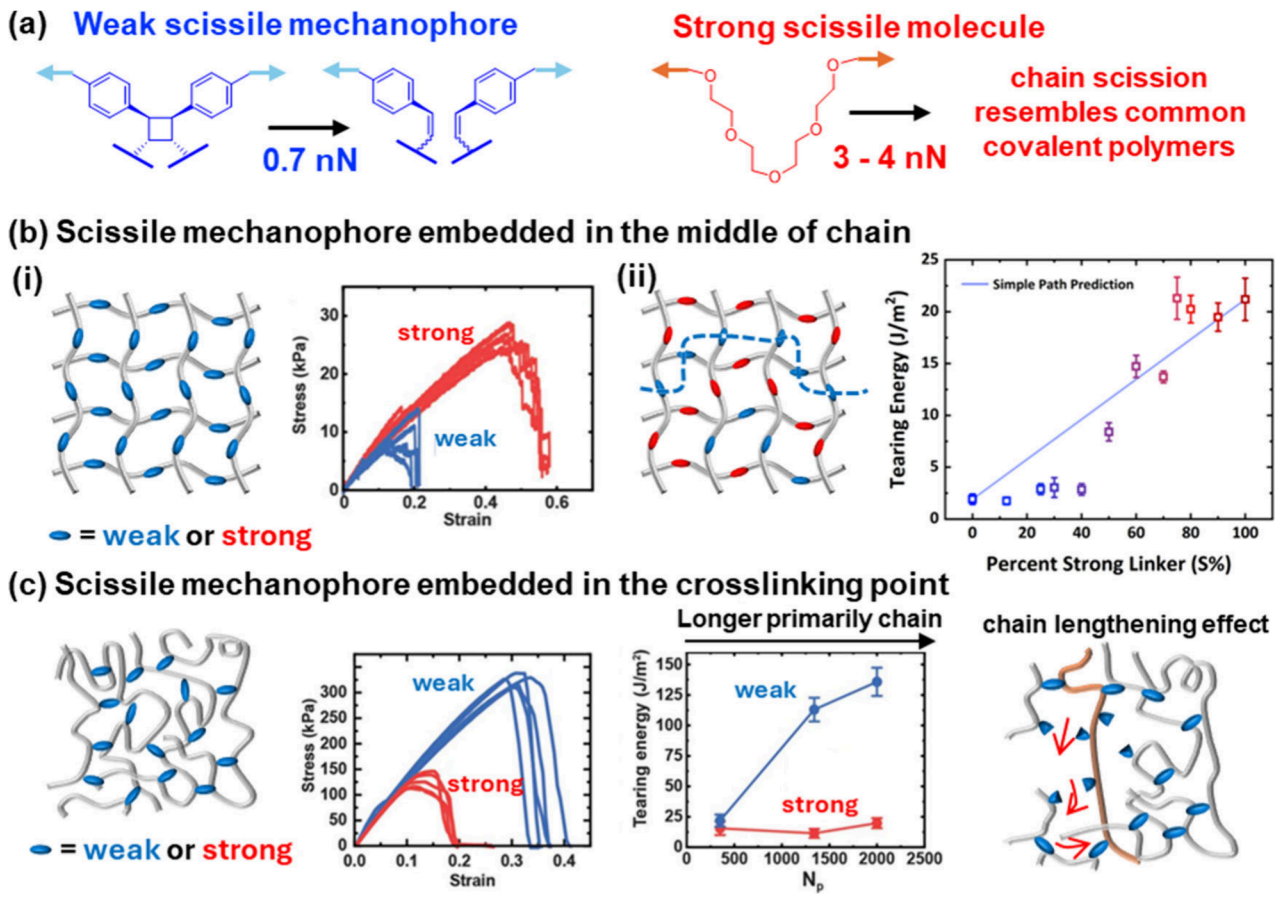

Figure 3. Influence of scissile mechanophore on the mechanical properties of various polymer network materials. (a) Mechanical activation behavior of weak scissile mechanophore versus typical strong scissile molecule. (b,c) Impact of the weak scissile mechanophore on polymer mechanical properties when (b) embedded in the middle of the primary chain within a homogeneous tetra-poly(ethylene glycol) network or (c) incorporated as the cross-linking point in an inhomogeneous network. Panel (b-i) and panel (c) are reproduced with permission from ref 54. Copyright 2023 The American Association for the Advancement of Science. Panel (b-ii) is reproduced with permission from ref 50. Copyright 2023 American Chemical Society.

nonscissile) and activation forces (Figure 2). When these mechanophores are incorporated into a single polymer chain, their influence on the force-stretch behavior of the chain is relatively well understood. However, the situation becomes much more complex when mechanophores are integrated into bulk polymer network materials. This complexity arises from the intricate polymer network structures, which lead to complex force distributions, bond scission, network structure alternation, and force redistribution during deformation. The mechanical effect of a mechanophore is not solely dependent on its mechanoresponsive behavior but also on polymer network structure, as well as the location and number of mechanophores within the network.

2.1. Scissile Mechanophore. Scissile mechanophores, such as cyclobutane,[64] azoalkane[60−62] and azobenzene,[51,65] break into two separate parts upon activation. In a conventional polymer chain, the chain ruptures when stretched to the activation force of the weakest bond near the chain contour length (Figure 2a,b). The incorporation of a scissile mechanophore with a lower activation force into the polymer chain results in chain rupture at a smaller displacement and lower force during stretching in single-molecule force spectroscopy (SMFS).[64] However, it is found that early rupture of the scissile mechanophore can either strengthen or weaken the bulk polymer mechanical properties, depending on the location of mechanophore in the network and network structure (Figure 3).

Craig's group embedded mechanically weak scissile cyclobutane mechanophores within a poly(ethylene glycol) (PEG) hydrogel by end-linking azide-terminated tetra-arm PEG with cyclobutane-containing bis-alkyne linkers[50,54,66] (Figure 3a). The resultant network is relatively homogeneous, with scissile mechanophores located in the middle of the elastic polymer strands (Figure 3b). Compared to tetra-PEG hydrogels end-cross-linked with a strong bis-alkyne without cyclobutane, the hydrogel with scissile mechanophore exhibits a similar swelling ratio and modulus, but much lower fracture strain and tearing energy. The weak bond, with an activation force only one-quarter that of the strong bond at the time scale of ∼0.1 s, leads to a 90% reduction in fracture energy. The authors further investigated the mechanical properties of gels cross-linked with a mixture of weak and strong linkers. Notably, the fracture energy is independent of the fraction of strong linkers when it is below 45% but increases steeply by 10-fold from 45% to 70%, and then plateaus, indicating a mechanophore reactivity-guided fracture pathway.[50]

Cao's group observed a similar trend, where weaker scissile mechanophores result in lower fracture energy when located in the middle of elastic polymer strands in a homogeneous PEG hydrogel.[51] They employed a scissile azobenzene mechano-

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phore, whose activation force for bond scission is photoresponsive. Under 365 or 435 nm light illumination, paraazobenzene predominantly adopts the cis or trans conformation, with rupture forces of ∼200 pN or ∼600 pN, respectively. As a result, the PEG single-network hydrogel and its associated double network hydrogels with cis-azobenzene under 365 nm light exhibits weaker fracture energy compared to the trans configuration under 435 nm, highlighting the potential of photoswitchable mechanophores for modulating the mechanical properties of hydrogels in response to light.

In contrast, when scissile mechanophores are embedded as cross-linking points in a randomly cross-linked network, an opposite effect has been observed: weak scissile mechanophores result in a tougher network (Figure 3c).[52−54] Craig's group synthesized elastomers via reversible addition−fragmentation chain-transfer polymerization of 2-methoxyethyl acrylate monomers with either cyclobutane-containing or non-cyclobutane-containing alkyl diacrylate cross-linkers. Despite having similar moduli, elastomers with weak linkers exhibited higher fracture energy and fatigue thresholds compared to those with strong linkers. Additionally, the toughening effect strongly relates to the primary chain length of the elastomers; longer primary chains amplify the toughness effect brought by weak scissile mechanophores. Otsuka et al. reported similar toughening effects in hydrogels and elastomers using different mechanically weak scissile mechanophores as cross-linkers.[52,53]

The weakening or toughening effects induced by scissile mechanophores arise from their selective scission activations, thereby altering the fracture pathway within the network.[50] Due to kinetic favorability, weak mechanophores with significantly lower activation forces compared to conventional strong bonds can be selectively activated in the polymer network. This has been confirmed through molecular dynamics simulations of network fracture[50] and experimental work by distinguishing bond rupture products from mechanophores and other nonspecific common bonds after stretching a double network (DN) hydrogel.[67] Notably, simulations of mechanophores positioned in the chain middle of a tetra-PEG single network show that a network with pure weak linkers has the same number of rupture sites as one with strong linkers, while a 1:1 mixture of weak and strong linkers results in twice as many bond breaks.[50] In contrast, experiments investigating mechanophores as cross-linking points in the first network of a DN hydrogel reveal that weak linkers cause more than five times as many bond ruptures, while a 1:1 mixture of weak and strong linkers exhibits a similar number of broken bonds as the pure weak linker.[60,67]

The differing effects of the same mechanophore in different network systems arise from its location within the network and the varying network alternation following its cleavage. When weak mechanophores are situated in the middle of a polymer chain, their cleavage causes the rupture of elastic chains, leading to early crack propagation. In contrast, when weak mechanophores are positioned at side-chain linking points as cross-linkers, scissile cleavage does not break the primary chain but instead lengthens it. This difference can trigger the activation of additional weak linkers in remote regions, dissipating energy and delaying fracture—somewhat analogous to the sacrificial bond effect observed with physical bonds such as hydrogen bonds, ionic interactions, and metal complexes,[68−70] as well as catch bonds.[71−73]

These results underscore the importance of considering the effects of mechanophores on polymer network materials from an integrated, spatiotemporal perspective. The impact of mechanophores on fracture energy cannot be fully explained by the Lake-Thomas theory,[74] which only accounts for energy stored in bridging strands. Recent models, such as the tree-like network model,[75,76] lattice-like network model,[77] and loop-opening models,[78] consider energy stored in tree-like structures and continuum regions, offering better predictions of intrinsic fracture energy and explaining the effects of weak mechanophores (Figure 4). Further research is needed to deeply understand how mechanophores and network structures influence local crack pathways, the number of bond rupture sites, and macroscopic materials properties.

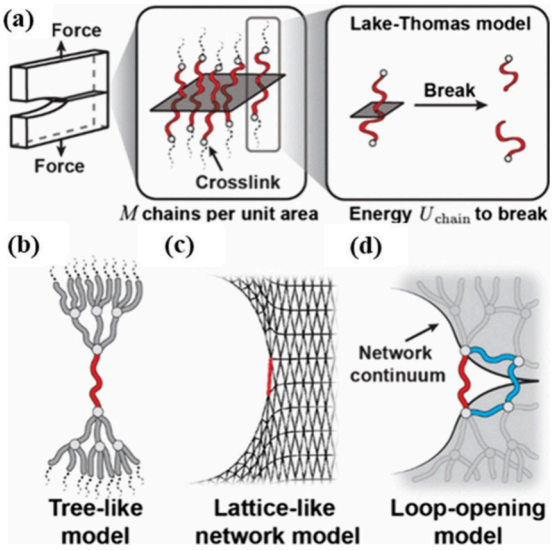

Figure 4. Schematic illustration of various models for the intrinsic fracture energy of the polymer networks. Adapted with permission from ref 78. Copyright 2024 American Chemical Society.

2.2. Nonscissile Mechanophore without Hidden Length. Common nonscissile mechanophores undergo a configuration change upon activation at lower forces while remaining intact. After activation, the new configuration does not significantly increase in length and behaves like strong molecules. A typical example is spiropyran mechanophore, which changes conformation and exhibits a color shift when activated. In SMFS, polymer chains containing these mechanophores show only a slight plateau after reaching the activation force, then behave similarly to conventional chains without mechanophores (Figure 2c).[79−81] This suggests that incorporating such mechanophores into a polymer network may not significantly alter the material's mechanical properties. To the best of our knowledge, no research has claimed that spiropyran significantly affects mechanical performance. For example, Creton's group synthesized multiple network elastomers, with the first network cross-linked by a mixture of spiropyran diacrylate and conventional 1,4-butanediol diacrylate cross-linkers, and found that spiropyran inclusion had minimal effect on mechanical properties (Figure 5a).[81] Ma and co-workers incorporated the benzimidazole-substituted spirolactam mechanophore into polyurethane and also observed that its introduction did not significantly alter the polyurethane's properties.[82]

2.3. Nonscissile Mechanophore with Hidden Length. To design nonscissile mechanophores capable of releasing hidden length upon activation, a scissile unit such as a

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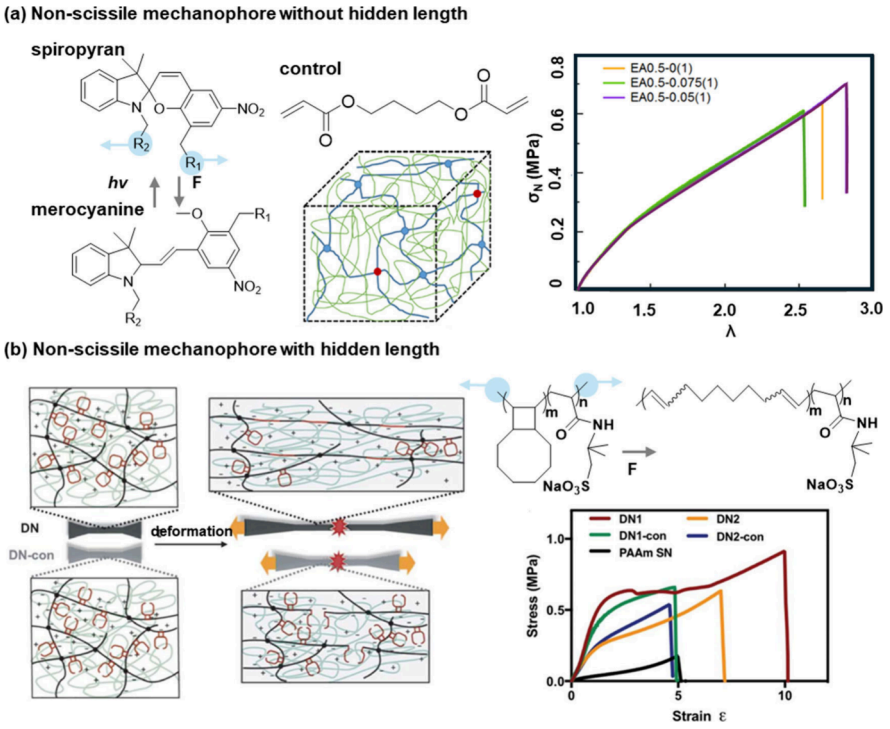

Figure 5. (a) Nonscissile mechanophore without hidden length, spiropyran, incorporated as cross-linking points in the first network of a double network elastomer, showing minimal impact on its mechanical properties. Reproduced with permission from ref 81. Copyright 2020 The American Association for the Advancement of Science. (b) Nonscissile mechanophore with hidden length copolymerized into the primary chain, enhancing the stretchability and toughness of DN gels. Reproduced with permission from ref 55. Copyright 2021 The American Association for the Advancement of Science.

cyclobutane mechanophore is often used to hold a long macrocyclic polymer chain, mimicking a polymer loop structure.[46,55,78,83,84] Upon activation of the scissile unit, the hidden length is released, increasing the contour length and enabling localized tension relief without chain breaking (Figure 2d). This results in a long plateau on the force−displacement curve in SMFS after activation, requiring more work to break the chain. Notably, mechanophores with hidden length are modified as acrylate monomers and incorporated into the backbone through copolymerization. This approach allows for multiple units with hidden length incorporated in the polymer chain, where successive activations of mechanophores can significantly increase the chain's contour length. Craig et al. incorporated such mechanophores with hidden length into the backbone of the first network of DN hydrogels and found that the fracture strain increased by about 50% and the tear energy improved by twice (Figure 5b).[55]

3. STRENGTHENING, GROWTH AND FUNCTIONALIZATION VIA FORCE-TRIGGERED BOND FORMATION

Another promising approach is to utilize force-induced bond scission products to trigger chemical reactions within the materials, enabling modification of the polymer network structure and properties. With a wide range of bond-scission products and resultant chemical reactions to choose from, this strategy offers limitless possibilities for realizing various mechanoresponsive functions. For example, it can lead to the strengthening, growth, and functionalization through force-triggered bond formation.

To mechanically strengthen the materials, the products of force-induced bond scission are designed to react with functional groups immobilized in the polymer chains, forming new cross-linking points in response to the force.[7−9,85,86] For example, Craig's group functionalized polybutadiene with a dibromocyclopropane mechanophore.[8] Activation of this mechanophore generates allylic bromides, which can be cross-linked in situ with carboxylates via nucleophilic substitution. Boulatov's group incorporated a spirothiopyran mechanophore into polyesters and polyurethanes. Activation of spirothiopyran generates a thiolate moiety, which can undergo rapid thiol−ene click reactions with reactive C═C bonds.[86] These mechanisms successfully strengthen the materials through force-triggered cross-linking reactions. However, they do not form new polymer chains or incorporate new functional molecules, limiting further enhancement of strength and functionalization.

In response, Gong's group has proposed a strategy to develop self-growing materials. These materials utilize force-induced bond rupture products to react with small molecules, forming new polymer chains or incorporating new functional molecules.[87] As a result, they can grow in volume, mass, and strength, and develop new functionalities in response to force, similar to living soft tissues. Specifically, they used force-induced mechanoradicals to trigger the polymerization of monomers, forming new polymer chains and new networks in DN gels. This mechanochemical growth mechanism enables DN gels to be mechanically strengthened, reshaped, and surface-patterned. Force-activated catalysts and enzyme systems are also promising for developing self-growing materials due to their ability to catalyze reactions efficiently with a small number of active species.[17,88−91] For example, Zheng et al. developed a mechanoresponsive biocatalytic hydrogel by controlling the interaction between the enzyme

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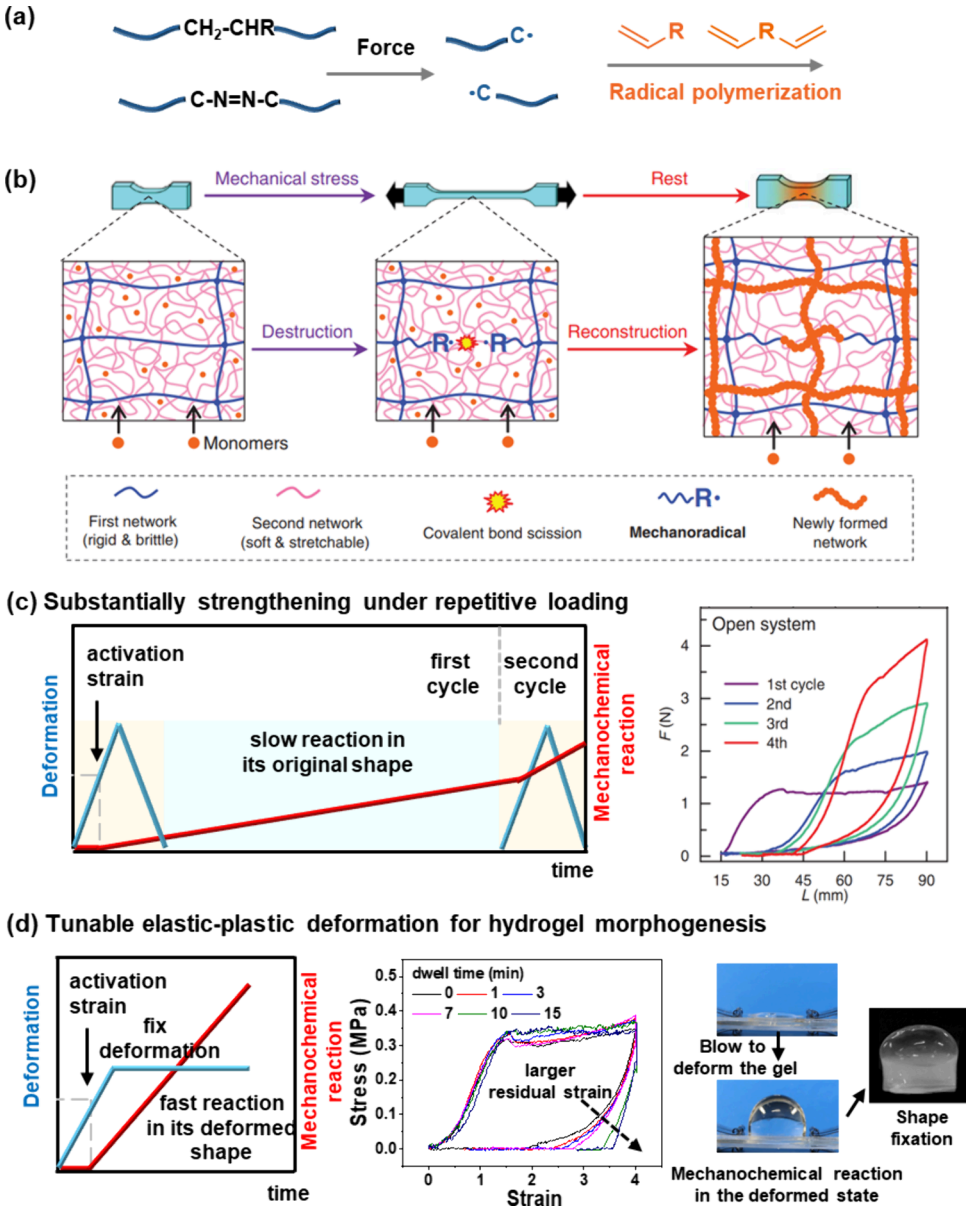

Figure 6. Various mechanoresponsive functions achieved in DN hydrogels by controlling the kinetics of force-induced chemical reactions and macroscopic material deformation. (a) Illustration of mechanoradical generation from homolytic chain cleavage and azoalkane activation, and its ability to trigger the polymerization of vinyl monomers. (b) Schematic illustration of DN gels undergoing force-induced destruction and reconstruction under external force. (c) Substantial strengthening through repetitive loading, with new network formation in its original shape. Reproduced with permission from ref 18. Copyright 2019 The American Association for the Advancement of Science. (d) Plastic deformation for hydrogel morphogenesis, achieved by controlling the formation of a new network in its deformed state. As the dwell time in the deformed state increased, the sample exhibited a larger residual strain, indicating enhanced plasticity. Reproduced with permission from ref 5 under Creative Commons Attribution-NonCommercial-NoDerivatives License 4.0. Copyright 2024 Z. J. Wang et al.

thrombin and its inhibitor hirudin.[17] Under external force, the noncovalent interaction between thrombin and hirudin is disrupted, exposing the enzyme's active site and allowing it to catalyze the formation of fibrin chains, which makes the hydrogels grow stronger. These studies offer valuable insights for designing self-growing materials. Since DN hydrogel has shown its great potential as a mechanoresponsive growing material, in the following section, we will use DN hydrogel as an example to discuss the design of self-growing materials and the key factors influencing their growth and functionality.

3.1. Double Network Hydrogels for Mechanochemical Growth. Mechanoradicals are among the most promising products of bond scission due to their universality and high reactivity. The homolytic cleavage of both natural and synthetic polymer chains, as well as the activation of radical-type mechanophores, generates radicals (Figure 6a).[18,56,57,60] These mechanoradicals are highly reactive, capable of undergoing oxidation−reduction reactions,[92] coupling with other radicals,[87] and, notably, inducing polymerization and cross-linking of vinyl monomers and cross-linkers. Even a small amount of mechanoradicals can lead to the formation of a large number of polymer chains and linking points through radical polymerization, compensating for the losses from bond cleavage.

To efficiently utilize bond-scission-induced chemical reactions, mechanical force should induce sufficient bond cleavage

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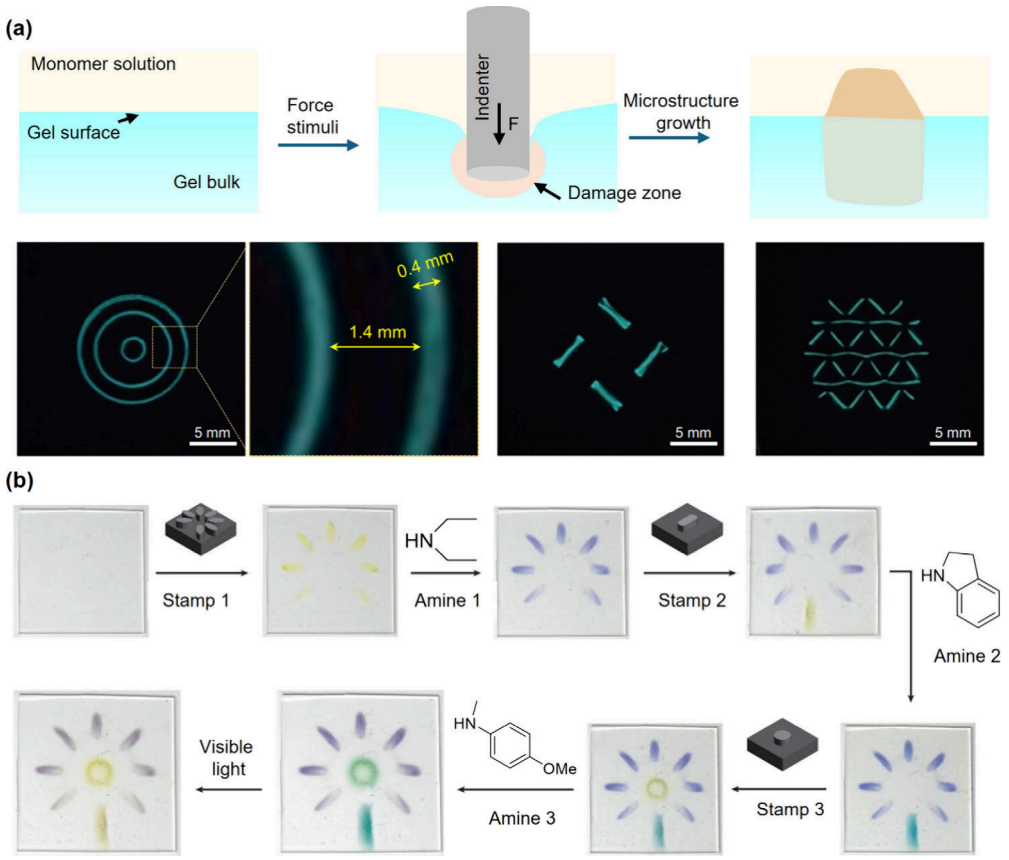

Figure 7. Mechanically induced surface patterning through spatiotemporal control of force. (a) Force-triggered rapid microstructure growth on the DN hydrogel surface. Reproduced with permission from ref 104 under Creative Commons CC BY license. Copyright 2022 Q. F. Mu et al. (b) Mechanochemical multicolor soft lithography on polydimethylsiloxane elastomer achieved via multiple localized compressions and subsequent reactions with different amines. Reproduced with permission from ref 105. Copyright 2023 Springer Nature.

within the material without causing catastrophic failure. This is particularly important when dealing with scissile mechanophores or mechanoradicals from polymer chain cleavage. Single network soft materials are often flaw-sensitive, where the breakage of even a few chains causes catastrophic failure due to stress concentration.[93] This makes it challenging to control bond rupture and obtain a sufficient number of activated bonds. Besides, these materials are often rubbery-like and their polymer chains are in a high entropy state,[94] making it difficult to transmit applied stress to the chemical bonds due to their rubber elasticity.

DN hydrogels offer an excellent solution for this issue.[95] DN gels consist of two interpenetrating polymer networks with contrasting mechanical properties: a brittle first network of relatively short polymer strands and a stretchable second network of long polymer strands (Figure 6b). With this structure, applied mechanical stress is predominately carried by the first network, which is in a highly prestretched, low-entropy state due to the great swelling during gel preparation.[96,97] It can effectively transmit macroscopic force to microscopic chemical bonds within the first network, facilitating the bond rupture and lowering the activation strain.[65,98] Meanwhile, the second network can pick up the stress unloaded by the bond breaking in the first network, reducing stress concentration and keeping material integrity.[99] Accordingly, this DN structure can allow for a much higher number of bond rupture events compared with a conventional single network material.[67] Due to these advantages, double network or multiple network materials are excellent materials to achieve mechanoresponsive functions.

3.2. Kinetics of Force-Induced Chemical Reaction and Deformation Effect. The strengthening effect is determined by the density of newly formed polymer chains or cross-linking points. Since the process involves force-induced bond scission followed by subsequent chemical reactions, the kinetics of these steps are critically important. If either process is too slow, the final strengthening effect may not be apparent within the desired time scale. Factors influencing bond scission kinetics include the polymer network structure and the mechanoreactivity of the bonds. For the subsequent reactions, key factors include the concentration of reactive species generated from bond scission and the concentration of other reactants. Unlike sonication, applying macroscopic mechanical forces such as stretching or compression introduces additional complexity due to factors like force-loading rate and material deformation. Controlling the state of deformation in which new bond formation occurs is crucial for designing mechanoresponsive materials. For instance, if the new network forms while the material remains in its original shape, the material can be strengthened while maintaining its initial shape. On the other hand, if the network forms in the deformed state, it can stabilize and fix the deformed shape.

In the initial work,[18] Gong's group demonstrated that DN hydrogels become repeatedly strengthened under repetitive loading through mechanoradical-triggered new network formation, which resembles to the mechanical training of

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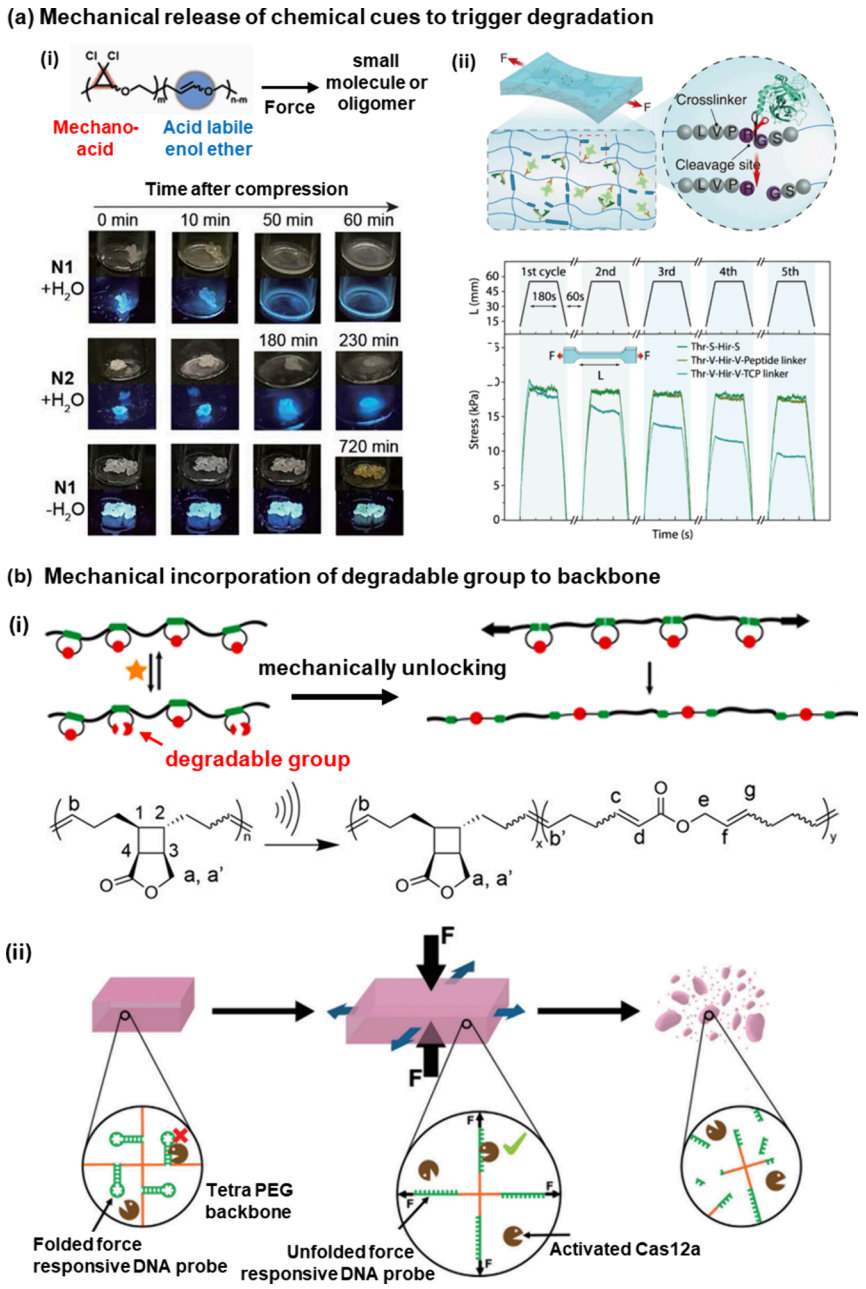

Figure 8. Strategies for leveraging force-induced bond rupture products to trigger polymer degradation. (a) Mechanically releasing chemical cues to induce degradation. (a-i) Mechanical activation of the mechanophore gem-dichlorocyclopropane generates HCl, accelerating the degradation of enol ester. Reproduced with permission from ref 22. Copyright 2024 American Chemical Society. (a-ii) Mechanically activated enzyme induces peptide cleavage, leading to repeated softening of the material under external force. Adapted with permission from ref 17 under Creative Commons CC BY license. Copyright 2024 K. Zhang et al. (b) Mechanically incorporating degradable groups into the polymer backbone. (b-i) Mechanical activation of a cyclobutane-fused lactone mechanophore introduces a degradable ester group into the main chain, making it responsive to chemical cues, while the polymer remains stable before force application. Adapted with permission from ref 108. Copyright 2020 American Chemical Society. (b-ii) Mechanical activation of DNA introduces enzyme-cleavable sites into the main chain, enabling degradation by the Cas12a enzyme. Adapted with permission from ref 24. Copyright 2023 Wiley-VCH.

muscles (Figure 6b,c). The DN gels are stretched far beyond the yield strain, at which the first network is broken into pieces to generate reactive mechanoradicals, then is immediately recovered to its original shape state. Mechanoradical polymerization and resultant new network formation occur in its original shape. As the reaction progresses, the density of newly formed network strands surpasses that of the broken ones. Consequently, in subsequent cycles, the gel exhibits increased mass, stiffness and toughness.[100,101] The strengthening effect strongly depends on the concentrations of the monomer and cross-linker supplied to the gel. By constructing channels inside the DN gels as a vascular-like circulatory system to deliver monomers, monomers can be continuously supplied to the gel, with their concentrations easily adjustable. This enables sustainable self-growth of hydrogels with tunable structures and mechanical properties in response to repetitive force application.[101]

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The concentration of the mechanoradicals is another key factor influencing the kinetics and performances of the new network formation. Due to the low concentration of radicals generated in a conventional double network with its first network cross-linked by a strong cross-linker *N,N′*-methylenebis(acrylamide), it takes tens of minutes to hours to form enough elastically effective polymer strands. This prolonged network formation time prevents real-time strengthening during deformation and makes it difficult for reinforcing crack resistance in materials, since cracks are prone to rapid propagation. To address this limitation, we adopted a mechanically weak azoalkane cross-linker in the first network, increasing the concentration of mechanoradicals by 5-fold.[60] The increased concentration of mechanoradicals accelerates the subsequent network formation rate and promotes the formations of a stronger network.

Inspired by biomorphogenesis guided by mechanotransduction,[102] recently we proposed that force-triggered network formation can also be used to alter the quasi-elastic deformation of the DN gel to plastic deformation by controlling the timing and deformation of polymerization (Figure 6d).[5,103] We stretched the gel at a fast-loading rate and maintained it in the deformed state, allowing the new network to form at its deformed state, rather than after it returned to its original shape. By extending the dwell time in the deformed state, a new network with sufficient strength forms, counterbalancing the retraction of the original network and permanently maintaining the deformed shape. This plasticity enables us to directly apply external forces to reshape the hydrogels into various configurations at room temperature, without the need for additional treatments.

3.3. Localized Growth and Functionality via Spatiotemporal Force Application. Apart from uniformly deforming a material, one can also control force distribution to selectively induce localized deformation and damage in DN gels. This allows for localized growth and functionality within the bulk or surface of gels. For example, Gong's group has used stamps or indenters to selectively compress DN gels, mechanically grafting fluorescent molecules and polymer chains with varying hydrophilicity or hydrophobicity (Figure 7a).[87,104] This process creates patterned surfaces for tailored functionality such as oriented cell growth and directional water droplet transport. Through multistep compression processes and reactions with different molecules, various functional groups can be incorporated into different parts of the material. For instance, Robb's group synthesized polydimethylsiloxane elastomer with a mechanophore that produces different colors upon activation and subsequent reaction with various amides (Figure 7b).[105] By applying multistep localized compression and amine reaction, multicolor images were printed onto the elastomer. The damaged zone area and depth resulting from localized compression or puncture are strongly influenced by the compression strain and the shape of the indenter. However, compared to uniaxial extension and uniform compression, the mechanics of localized compression and puncture are relatively poorly understood, largely due to the heterogeneous, strongly localized, and nonlinear deformation fields.

4. DEGRADATION VIA FORCE-INDUCED EXTENSIVE BOND CLEAVAGE

Another promising application of polymer mechanochemistry that has garnered great attention is force-triggered polymer degradation. Degradation is crucial for both reducing waste accumulation in the environment and for its use as degradable materials in biomaterial fields. Using mechanical force to trigger degradation offers precise control over the timing and location of the breakdown process, enabling targeted material degradation when and where needed.[27,28,106−109] Additionally, it eliminates the need for additional chemical signals, which may be unsuitable for certain sensitive applications. However, applying macroscopic force or ultrasound often results in only partial polymer chain scission and does not achieve complete degradation. Macroscopic mechanical force can fail to maintain pressure once the material is compromised, while ultrasound may become ineffective as polymer chain length becomes small.[110] To overcome these limitations, various strategies have been proposed to enhance the degradation process, facilitating a more controlled and extensive breakdown of polymer materials.

One approach involves separately incorporating degradable functional units and mechanophores into the polymer backbone, where activation of the mechanophores releases chemical cues to trigger degradation (Figure 8a).[19−22] A recent example reported by Craig's group[22] features a polymer network with an acid-sensitive, hydrolytically unstable enol ether and a mechanophore, gem-dichlorocyclopropane (gDCC) (Figure 8a-i). When activated under sonication or compression, gDCC releases HCl, which then catalyzes polymer breakdown at the enol ether sites. After compression, the polymer network with gDCC dissolved three times faster than the control network without gDCC. The previously mentioned mechanoactivated catalytic activity of the enzyme thrombin system[17] can also be employed to achieve mechanodegradation by incorporating thrombin-degradable peptides into a hydrogel network (Figure 8a-ii). Under repetitive mechanical stretching, the hydrogel exhibits a significant reduction in mechanical properties due to the cleavage of thrombin-cleavable peptide cross-linkers. However, a notable issue with this route is that preincorporated degradable functions, such as ester groups, can degrade prematurely due to thermal, acidic, or enzymatic hydrolysis under ambient conditions. This results in continuous chain cleavage and unexpected decreases in mechanical properties before the intended degradation, which contributes to the poor thermal and UV stability of degradable polymers.

To tackle this challenge, mechanophores are designed to act as gates that control the exposure of degradable functional groups within polymer backbone (Figure 8b).[27,28,107−109] Initially, these degradable groups are either located in side-chains or not present at all. Only after mechanophore activation, degradable groups from the side chain or from the activated mechanophore can be incorporated into the polymer backbone. This design ensures that the material remains highly stable until degradation is triggered on-demand. Several sophisticated examples of mechanically gated degradable polymers have been reported. However, these studies often demonstrate degradation only in polymer solutions under sonication. For instance, Wang's group synthesized a polymer with cyclobutane fused-lactone mechanophores in each repeat unit (Figure 8b-i).[108] Prior to mechanoactivation, the polymer backbone showed excellent hydrolytic stability, even when exposed to a strong base that typically hydrolyzes lactones. After 4 h of ultrasonication, the molecular weight of the cyclobutane-lactone polymer decreased from 105 kDa to 35 kDa, with 48% of the cyclobutane units activated,

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introducing degradable ester groups into the backbone. Subsequent treatment with the organobase tetrabutylammonium hydroxide led to small molecule degradation and a reduction in polymer chain length to 16 kDa.

One successful example of mechanically gated degradation in bulk materials is reported by Salaita's group (Figure 8b-ii).[24] They synthesized a tetra-PEG hydrogel cross-linked with folded DNA and doped with nucleases. In their design, the nucleases could not cleave the folded DNA cross-linkers without applied force. When piconewton forces were applied, the DNA linkers unfolded, exposing enzymatic cleavage sites and resulting in mechano-induced degradation. Their experiments demonstrated that the hydrogel underwent complete degradation within 3 h under continuous compressive force, which was significantly faster than degradation without force application. However, the folded DNA still exhibited some degradation even in the absence of mechanical force. This partial degradation undermines the intended advantage of mechanically gated degradation.

The kinetics of force-induced degradation are crucial, particularly for materials used in tissue engineering and drug release. A key factor is still the number of activated mechanophores under external force, which directly influences degradation rates. However, research in this area remains limited, especially for bulk materials, and more effort is needed to fully understand and optimize these processes.

5. SUMMARY AND OUTLOOK

Beyond traditional applications such as damage detection or small molecule release, polymer mechanochemistry has emerged as a transformative method for mechanically remodeling the polymer structure and properties to meet diverse requirements across various fields. In this Perspective, we review latest progress in polymer mechanochemistry for on-demand polymer network materials. We believe that double network hydrogels provide an excellent material platform for polymer mechanochemistry. Their contrasting double network structures ensure that macroscopic stresses are effectively transferred to the polymer chains and their chemical bonds of the targeted first network, thereby effectively activating chemical reactions. The high permeability of the hydrogel facilitates the supply of reactants and the removal of products and wastes. Double network hydrogels have the potential to develop "living" materials through the growth and degradation of polymers. Similar to stem cells that differentiate into different cells with specific functions, double network hydrogels can act as "stem materials" that can adaptively change their size, shape, and function over time in response to force and environmental cues. Exploring this new field of soft materials have many challenges. One core challenge is the understanding of the fundamental mechanisms. While the basic principle involves bond scission triggered by mechanical forces, several critical questions remain unanswered. These include how forces are distributed across different polymer network architectures, how these forces lead to bond rupture with or without the presence of mechanophores, and how the force is redistributed after bond scission.[93,111] Additionally, the transition from microscale bond rupture to macroscale material failure is not fully understood. The relationship between macroscopic forces, mechanophore reactivity, and bond rupture kinetics within the bulk materials needs further elucidation. When bond rupture products are used to initiate further reactions, the kinetics of these subsequent chemical processes are crucial, particularly given that the bond rupture sites are immobilized in broken polymer chains and the reactions are affected by network deformation. Addressing these questions requires a concerted effort involving experiments, theory,[112] and simulations[111] to tackle these complex challenges and guide the design of materials and mechanophores for new functions along with required mechanical properties.

Additionally, the practical application of polymer mechanochemistry often faces challenges related to the use of mechanophores and complex material systems. Mechanophores typically require intricate synthesis processes, which can be costly and difficult to integrate into common polymers. There is a need to explore more accessible mechanophores that can be easily incorporated into widely used materials. Directly utilizing mechanoradicals generated from bond rupture in the polymer main chain offers a more straightforward solution. Besides, achieving force-triggered chemical reactions often necessitates the inclusion of additional reactive components, such as vinyl monomers, which can compromise the material's long-term stability and limit their suitability for biological applications. To address these issues, immobilizing reaction sites within the material and incorporating biocompatible building blocks, such as amino acids, proteins, and enzymes, could offer viable solutions and expand the practical use of polymer mechanochemistry.

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Notes

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Jian Ping Gong is a distinguished professor of Hokkaido University. She graduated from Zhejiang University, and received Doctor of Engineering at Tokyo Institute of Technology. She joined the faculty at Hokkaido University in 1993. She received many awards, including Wiley Polymer Science Award (2001), the DSM Materials Sciences Award (2014), the Chemical Society of Japan Award (2022), and the APS Polymer Physics Prize (2023). Her research interests include tough double network hydrogels, hydrogel friction and adhesion, hydrogel composites. Recently, she is also interested in self-growing hydrogels based on mechanochemistry.

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