Macromolecules

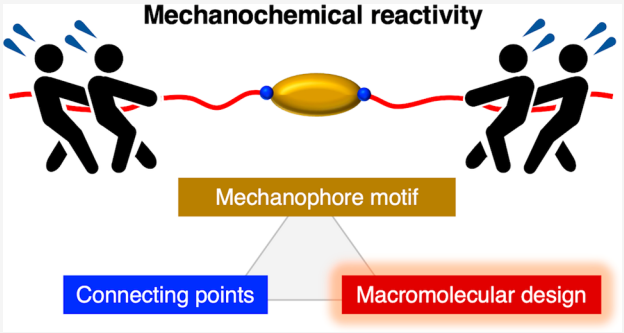
pubs.acs.org/Macromolecules
Perspective

Enhancing the Reactivity of Mechanically Responsive Units via Macromolecular Design

Takuma Watabe and Hideyuki Otsuka*

Cite This: *Macromolecules* 2024, 57, 425−433

ABSTRACT: The field of polymer mechanochemistry has experienced a rapid growth in the past two decades because of the establishment of the concept of mechanophores, which describes mechanically active molecular units. A wide variety of mechanophore functions have been developed, and these are expected to evolve into practical applications. In particular, self-reporting mechanochromism in glassy polymers, thermoplastic elastomers, and polymer networks has been extensively explored. However, owing to the low reaction efficiency of mechanophores in bulk materials, the induced property changes are restricted to optical properties. Recent studies have revealed that the macromolecular design contributes more substantially to the mechanochemical sensitivity and efficiency than the fine-tuning of the mechanophore structure itself. This Perspective aims to provide an overview of strategies based on the macromolecular design to transfer force efficiently to mechanophores through polymer chains.

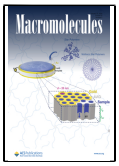


1. INTRODUCTION

Exposure to forces causes changes in the position or state of matter. In particular, the conformation, bond angle, and bond length of polymers change upon exposure to an external force, which is the origin of the viscoelastic behavior that is unique to polymeric materials.[1] When the external force is sufficiently high, irreversible destruction of the macromolecule occurs, which goes beyond the scope of polymer physics, reaching the field of polymer mechanochemistry. Given that repeated or excessive force causes material deterioration or destruction, a deep understanding of the molecular behavior of materials under mechanical stress is essential to improve their toughness and lifetime. However, polymeric materials are complex systems with structural and spatial inhomogeneities that range from the nano- to mesoscale, such as heterogeneous chain-length distribution, entanglements, loops, dangling chains, phase separation, and crystallinity, which hinder gaining a precise understanding of their response to external forces.[2,3] In this context, the introduction of the concept of mechanophores by Moore in 2007 enabled the molecular-level observation and utilization of an applied force.[4] Mechanophores generally contain mechanically weak chemical bonds that can be selectively cleaved to produce valuable chemical species. Depending on the type of mechanophore, a wide variety of functions have been realized, i.e., color change,[5−16] small-molecule release,[17−22] metal−catalyst generation,[23−27] energy dissipation through the stretching of hidden length,[28] accelerated degradation,[29−32] and mechanical cascade reactions for mechanically induced strengthening.[9,33−36] Moreover, research in this area has uncovered that mechanochemical reactions can yield products different from those obtained via thermal reactions[37,38] or provide access to conjugated polymers that cannot be synthesized using conventional methods.[39−41] Therefore, the rapid progress in the field of polymer mechanochemistry can be exploited in diverse areas, including polymer synthesis, functional materials, and biomedical fields.[42−45]

Mechanophores with diverse functions have been extensively explored in solution systems, which exhibit high reaction efficiency and can be easily analyzed. In contrast, reports describing functions other than mechanochromism in bulk systems are comparatively scarce, despite the inherent interest and practical value of realizing mechanoresponsive functions in the bulk. This is because the low reaction efficiency of mechanophores hinders achieving substantial changes in the physical properties. For example, although intense research efforts have been devoted to extending the lifetime of materials through reinforcement of damaged areas via mechanically induced strengthening, no satisfactory results have been achieved to date.[33−35]

Received: June 29, 2023
Revised: December 9, 2023
Accepted: December 12, 2023
Published: January 3, 2024



https://doi.org/10.1021/acs.macromol.3c01280
Macromolecules 2024, 57, 425−433

In 2019, Gong et al. developed an artificial double-network hydrogel that grows under mechanical loading like a muscle without relying on mechanophores. Monomers as solvents polymerize from mechanoradicals generated inside the gel, forming a new network and gaining weight and mechanical strength.[46] Because a sufficient number of mechanoradicals are generated via the cleavage of covalent bonds in the stretched first network, a sufficient amount of network is newly formed to reinforce oneself, which stands in contrast to the macroscopic destruction that progresses easily in conventional single networks.

Meanwhile, mechanically induced consecutive reactions using mechanophores rely on a very small number of active species because stress concentrates on a small part of polymer chains, resulting in low levels of activation. To circumvent this issue, many studies have realized that the force required for activation is tuned by modifying the electronic state of mechanophores or their bonding position within the polymers;[47−52] nevertheless, a drastic improvement in the reactivity has rarely been achieved in the solid state (Figure 1). Conversely, the macromolecular

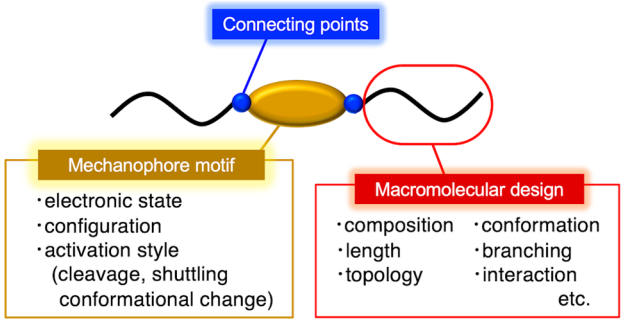


Figure 1. Factors affecting the mechanophore responsivity.

structure of a polymer connected to a mechanophore is known to be a major determinant of the mechanochemical reactivity. Unfortunately, useful findings are limited due to the large number of variables, the complexity of the polymer design, and the difficulty in experimental and computational analysis. Herein, aiming to pave the way for an optimal macromolecular design to realize novel mechanoresponsive functionalities and their application in practical materials in the near future, we provide an overview of studies that focus on the macromolecular design in order to optimize the mechanoresponsive properties of polymers.

2. MACROMOLECULAR DESIGN IN POLYMER MECHANOCHEMISTRY (SOLUTION vs SOLID)

It is well-known that chemical reactions in polymers generally exhibit lower reaction rates than those involving small molecules due to significant steric hindrance and slower diffusion. On the other hand, mechanochemical reactions are more active in polymer systems because the polymer chain works as a force-transmitting medium. Therefore, an appropriate design of the polymer chains can improve the sensitivity and efficiency of mechanochemical reactions without tuning the electronic state. In fact, many stimuli-responsive small molecules behave as mechanophores when they are embedded in polymer chains. In solution-based mechanochemistry, highly dilute solutions are generally subjected to ultrasonic treatment, and the reaction rate is determined by the power of the ultrasound, type of solvent, temperature, and concentration.[53] In contrast, mechanical energy can be applied to polymer materials using various methods, including pulverization, stretching/compression, and kneading. Moreover, the mechanical response of viscoelastic polymers largely depends on the environmental temperature and strain rate, greatly expanding the influencing factors. Given the complex interactions between polymers, the reactivity of bulk polymers is different from that of solution systems, where it is feasible to assume that the polymer exists in the form of single chains. As a typical example, the rate of mechanochemical chain scission during ultrasonic irradiation is solely governed by the end-to-end length of the polymer, regardless of the presence of slight differences in the side-chain structure[54] or the existence of arms.[55] In contrast, both the arm length and the number of branches determine the mechanical reactivity during the milling of mechanophore-centered polymers.[56] It is thus assumed that the force can be transmitted more efficiently with increasing number of arms due to the entanglement among polymer chains. While polymers with a single mechanophore in the center allow us to easily analyze the reaction, we may struggle with the low mechanophore content. Accumulating multiple mechanophores on a single chain is a straightforward approach to enhancing mechanochemical response. However, as for polymers with multiple scissile mechanophores in the main chain, mechanophores become inert to forces once the main chain is ruptured to get the total main chain length below the limiting length. Therefore, a nonscissile design in which scissile parts are tethered to macrocycles is required to show a continuous response to mechanical input.[57] As another example, Weng et al. accomplished both high conversion and high mechanophore content through bottlebrush polymers containing multiple scissile mechanophores at the root of graft chains because the scission of mechanophore does not damage the main chain.[58] Polymer architecture is no longer limited to linear ones, bottlebrushes, macrocycles, etc.; micelles and microgels are also the targets of mechanochemistry in solution,[59−61] which also allow us to increase the number of activation events.

Peterson et al. have deepened the understanding of the mechanical reactivity determined by polymer structures both in solution and in the solid state.[62−64] They explored the mechanochemical reactivity of a variety of chain-like polymers with or without mechanophores, including bottlebrush and dendronized polymers, revealing that the rate constants of the degradation during ultrasonication can be fitted to a master curve using the natural log of persistence length or the square root of the monomer molecular weight, as long as the chemical structure of the backbone is preserved (Figure 2).[63] They also found a linear relationship between the initial glass-transition temperature and the rate of mechanochemical degradation of general amorphous polymers subjected to ball milling.[64] Although a determining factor for the reaction rate has not been identified yet, the ball-milling degradation of bottlebrush polymers and dendronized polymers is known to be accelerated upon increasing the length of both main and side chains.[63] It can be qualitatively interpreted that this is because the extension of the side chains increases the conformational restrictions (i.e., rigidity) of the main chain. In addition to those described here, the structure−reactivity relationships regarding topologically complex polymers such as cyclic, dendritic, and intermolecularly cross-linked polymers have been investigated. We will not go into details in this Perspective; please refer to the recent Feature Article.[65]

https://doi.org/10.1021/acs.macromol.3c01280
Macromolecules 2024, 57, 425−433

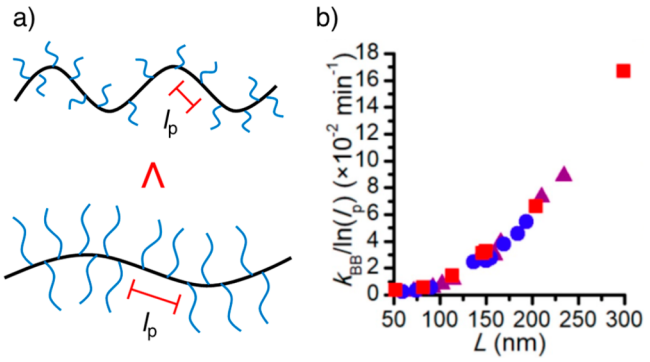


Figure 2. Comparison of the mechanochemical reactivity under ultrasonication. (a) The rate of backbone scission (k_{BB}) increases following the increase in the chain rigidity, or persistence length (l_p), when sterically crowded side chains are connected. (b) Master curves of $k_{BB}/\ln(l_p)$ plotted against the contour length (L) for three different bottlebrush and dendronized polymers. Reproduced with permission from ref 63. Copyright 2021 Wiley-VCH.

3. THERMOPLASTIC ELASTOMERS

Thermoplastic elastomers are practical polymer materials in which mechanoresponsive properties can be incorporated.[66] With regard to thermoplastic elastomers, the introduction of polar groups that induce strong intermolecular interactions is an effective approach to improve the mechanophore reactivity. In a representative study, Weng et al. have reported that the introduction of ureidopyrimidinone (UPy) skeletons, which form strong quadruple hydrogen bonds, into linear polyurethane containing spiropyran (SP) results in deep mechanochromism due to an increase in chain orientation and subsequent strain-induced crystallization (Figure 3a).[67,68] However, the strong hydrogen bonds between UPy considerably improve the macroscopic mechanical properties; therefore, this design is not suitable for evaluating the effect of the introduction of polar groups on the mechanochemical reactivity.

To address this issue, Sijbesma et al. have incorporated a mechanochromic component (33.3 wt %), which comprised a segmented polymer that contains a bis(adamantly)dioxetane mechanophore with distinct hard segments, into a matrix of nondoped polyurethane.[69] Even though the macroscopic mechanical properties did not change substantially after introducing the mechanochromic component, the total light intensity emitted upon elongation steadily increased due to an increase in the molecular weight and the strengthening of the hydrogen bonding within the hard segments (Figure 3b). This study also disclosed that an increase in the strain rate of thermoplastic elastomers leads to stronger mechanoluminescence. These observations suggest that a large local force is generated to activate mechanophores through the inhibition of chain relaxation via conformational rearrangement and disentanglement. Meanwhile, in some polymer designs, a lower strain rate is conducive to the mechanical and mechanoresponsive properties because an appropriate rearrangement of hydrogen bonds facilitates the segment/chain orientation.[70]

4. CROSS-LINKED POLYMERS

Cross-linked polymers can undergo relatively efficient mechanochemical reactions compared to linear systems because stress is mainly concentrated at the cross-linking points. Binder et al. have indirectly evaluated the relationship between the polymer structure and the reaction efficiency by mechanochemically activating Cu−bis(*N*-heterocyclic carbene) mechanophores followed by a Cu(I)-catalyzed click reaction to generate fluorescent molecules (Figure 4a).[71] Upon subjecting a mixture of mechanophores and reactants dispersed in a poly(tetrahydrofuran) matrix to compression cycles, the conversion of the click reaction gradually increased until reaching a plateau. The study revealed that the incorporation of mechanophores into a long polymer chain or a polymer network enables a more efficient mechanochemical reaction (Figure 4b). Saito et al. have clearly demonstrated that mechanochemical reactions during the elongation of elastomers proceed more efficiently at the

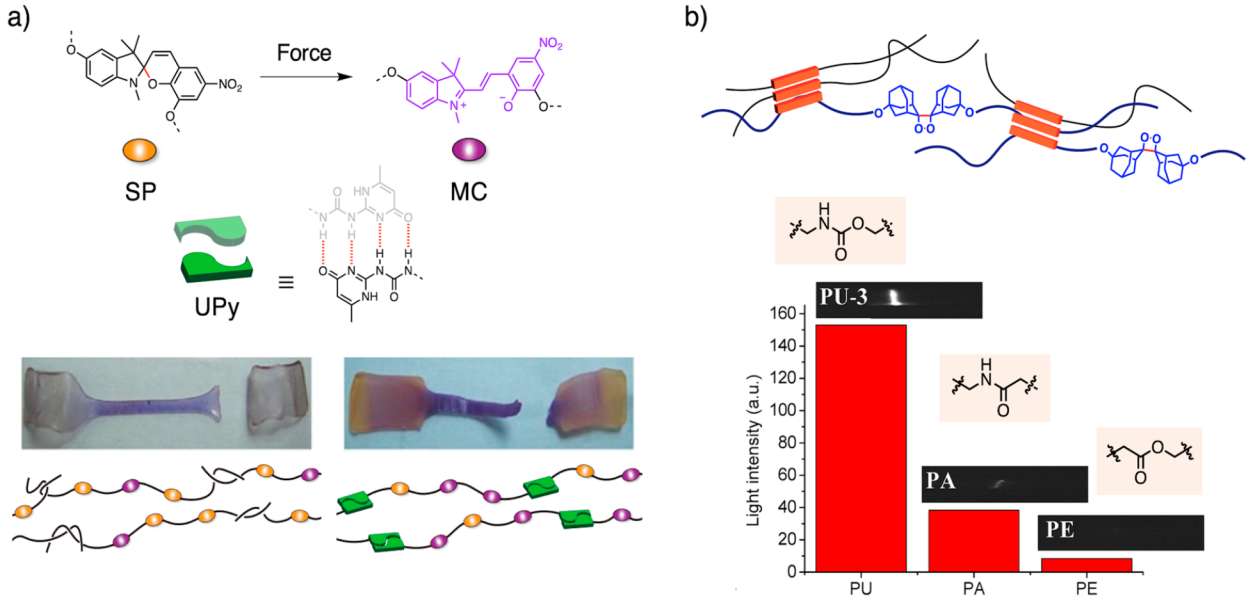


Figure 3. (a) Optical images of fractured polyurethane elastomers that bear spiropyran (SP) mechanophores end-capped with ureidopyrimidinone (UPy) or urethane. (b) Optical images and the corresponding cumulative light intensity from a 1,2-dioxetane mechanophore in thermoplastic elastomers with different interactive blocks under tensile deformation. Reproduced with permission from refs 67 and 69.

https://doi.org/10.1021/acs.macromol.3c01280
Macromolecules 2024, 57, 425−433

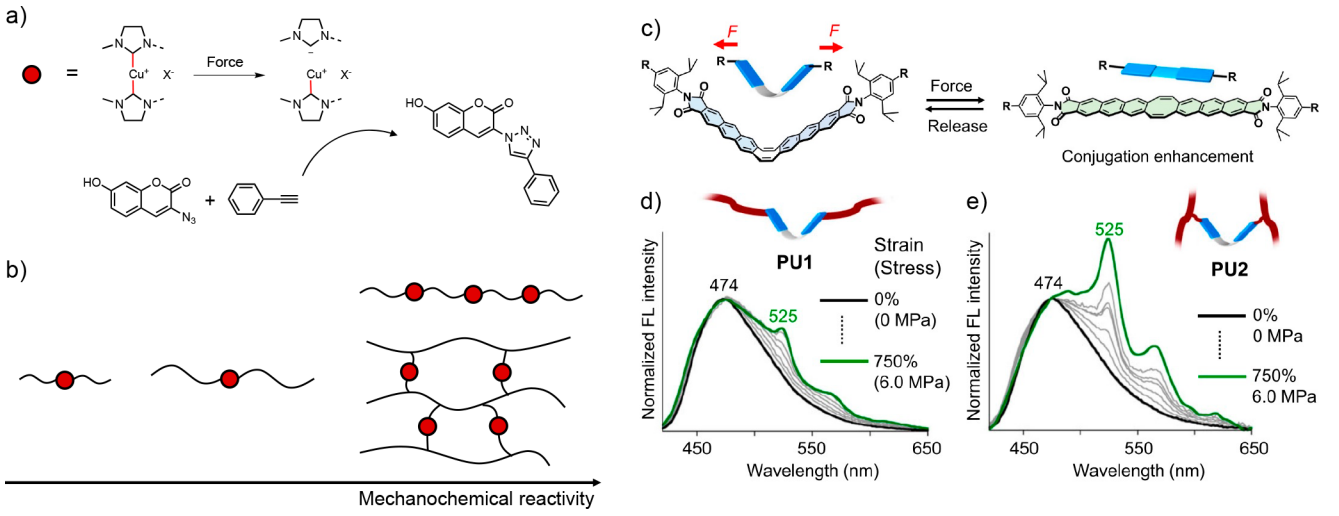


Figure 4. (a) Mechanochemical activation of Cu−bis(*N*-heterocyclic carbene) mechanophore and successive fluorogenic click reaction for quantitative evaluation. (b) Order of the mechanochemical reactivity for different macromolecular designs. (c) Chemical equilibrium of a flapping mechanophore that enables fluorescence changes in response to a relatively weak force. Change in the fluorescence spectra under elongation of polyurethane elastomers in which the mechanophore is doped at (d) the main chain and (e) the cross-linking points. Reproduced with permission from ref 72. Copyright 2022 Nature.

cross-linking points than at the main chains.[72] When a trace amount of a flapping mechanophore (Figure 4c) was doped into the main chain or the cross-linking points of poly(urethane) networks, the activation percentage at the cross-linking points was about twice that at the main chain (Figure 4d,e), while their macroscopic stress−strain curves completely overlapped. A very recent paper examined how the molecular length of a mechanophore strand in a PDMS network affects the activation sensitivity but a spacer of ∼50 atoms made little change in the macroscopic mechanochromic properties.[73]

In polymer composites, the local force reaches a maximum value at the interface between the polymer matrix and the filler. Our group has already reported that polymer−silica composites that contain diarylbibenzofuranone (DABBF), a dynamic covalent mechanophore, undergo efficient mechanochemical reactions through effective force propagation and inhibition of the radical recombination at the interface.[74,75] Afterward, Sottos et al. have demonstrated that SP immobilized at the interface between poly(methyl acrylate) and silica nanoparticles exhibits greater mechanical reactivity than that functionalized in the bulk; specifically, a smaller deformation is required to induce the fluctuation of the optical properties, and a higher conversion of SP to the merocyanine form is achieved.[76]

The magnitude of the force exerted on a polymer chain is given by the ratio of the spatial end-to-end distance to the contour length, i.e., chain length at maximum extension (Figure 5). In particular, a single polymer chain experiences low stress at low strains because the entropy loss is small in the early stage; however, the force exponentially grows as it approaches a finite extensibility of polymer chains.[77] The activation of mechanophores generally occurs around the finite extensible length because the cleavage of covalent bonds in mechanophores requires a force of at least 200 pN,[78,79] which falls within the stiffening region. Therefore, a macromolecular design that allows more molecular chains to be fully extended will be effective in improving mechanophore reactivity. Polymer networks inevitably contain defects such as dangling and loop chains, which serve as elastically ineffective chains.[80] As a typical example, nanogels that are formed in the early stage of free-

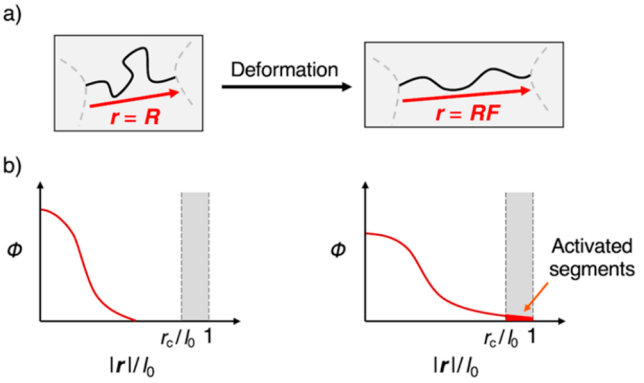


Figure 5. (a) Schematic of a change in the conformation of a polymer segment. (b) Existence probability (φ) of the one-dimensional end-to-end vector of a segment in an ideal polymer network. Here, l_0 and r_c represent the contour and critical length for the mechanochemical reaction, respectively.

radical polymerization are linked to each other through the remaining functional groups, and the strands that connect the nanogels work as elastically effective chains. The cross-linking heterogeneity leads to a broad distribution of the segment length. Short chains largely contribute to the mechanical properties, thus playing an important role in mechanochemistry.

Considering a single polymer strand in a network with a contour length l_0 and initial end-to-end vector $\boldsymbol{r} = \boldsymbol{R}$ (Figure 5a), the distribution of an end-to-end vector $\varphi(\boldsymbol{r})$ can be described by a Gaussian distribution under the ideal model assuming that the exclusion-volume effect does not exist (Figure 5b). When a polymer network is subjected to a macroscopic deformation $\boldsymbol{F}$, the end-to-end vector changes into $\boldsymbol{r} = \boldsymbol{R}\cdot\boldsymbol{F}$ according to the affine network model. The distribution of the vector broadens through deformation, eventually damaging the polymer chains, or via activation of mechanophores by approaching the fully stretched conformation.[81] In order to realize efficient mechanochemical reactions, the portion of polymer chains that exceed the limit of stretching should increase. To this aim, improving the extensibility of polymer networks to increase the

https://doi.org/10.1021/acs.macromol.3c01280
Macromolecules 2024, 57, 425−433

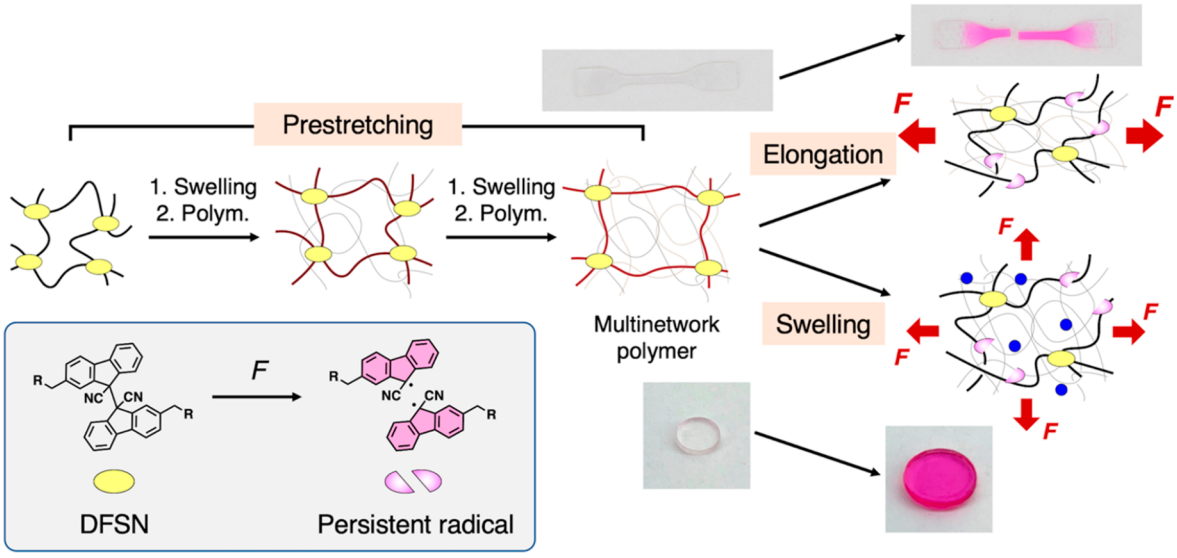


Figure 6. Mechanically sensitive polymer networks based on a multinetwork strategy and a DFSN mechanophore. The multinetwork polymer demonstrates outstanding mechanical response to uniaxial elongation and isotropic expansion during swelling. Reproduced with permission from refs 88 and 90. Copyright 2023 Wiley-VCH.

vector F can be regarded as the simplest approach. However, the extensibility is not easily tunable because it is inherent to the polymer species or composition. The threshold of activation strain remains as high as 100%,[50,82−84] indicating that functionalities such as mechanochromism can be observed only immediately prior to material destruction.

Another approach to facilitating mechanochemical reactions is expanding the initial distribution of $\varphi(r)$; namely, polymer strands are fixed at a strained conformation in the initial state. Preorientation of molecular chains during sample preparation is a relatively straightforward and general strategy to realize an efficient mechanophore activity and to reduce the threshold deformation for mechanophore activation. To achieve this, the designed material should contain polymer strands fixed at the stretched state, which is entropically unfavorable. For example, a composite material based on mechanophore-containing oriented fibers in a polydimethylsiloxane (PDMS) matrix exhibits highly sensitive mechanochromism at strains as low as 10%.[85] In addition, elastomers exhibiting anisotropic mechanochromism have been achieved by controlling the fiber orientation in a uniform direction. The study conducted by Sottos et al. also revealed that the orientation of mechanophores in the elongation direction is important for mechanical activation, utilizing fluorescence anisotropy of mechanically activated spiropyrans.[86]

In cross-linked polymers, the sensitivity of mechanophores has been increased via molecular stretching due to swelling. For example, Qiao et al. have successfully reduced the strain and energy required for mechanochromism under uniaxial elongation by prestretching the molecular chains through a stepwise swelling and cross-linking process, i.e., a multinetwork (MN) strategy.[87] The first network doped with SP mechanophores is expanded via monomer swelling, and the isotropically stretched network structure is fixed after the polymerization. By taking advantage of the quantitative feature of the stable radicals generated from a difluorenylsuccinonitrile (DFSN) mechanophore, our group has demonstrated that the MN strategy boosts the amount of mechanically active mechanophores, even though the mechanophore is substantially diluted in the matrix networks (Figure 6).[88] In addition to its mechanochromic properties, DFSN functions as a sacrificial bond[89] because it is weaker than a typical covalent bond, resulting in an improvement in the mechanical properties of the elastomer. Moreover, the polymer network cross-linked by DFSN with increased mechanosensitivity responds to the force arising from solvent absorption.[90] Solvent swelling induces an efficient mechanochemical reaction compared to one-dimensional elongation because it provokes an isotropic expansion of the network, while the uniaxial stretching of elastomers is accompanied by compression in the direction perpendicular to the loading direction. Because of its versatility, this strategy has lately attracted increasing attention and has been applied to a wide variety of reaction systems.[91−96] Moreover, the mechanochemical sensitivity can be enhanced simply by solvent swelling at the expense of the mechanical performance.[97]

As discussed above, the scission, or sometimes releasing hidden length, within mechanophores can effectively dissipate elastic energy to reinforce gels and elastomers. Recent notable work from Craig's group demonstrated that the sacrificial species make networks either tougher or weaker, depending on their positions.[98−100] Tetra-arm poly(ethylene glycol) gels get weaker when mechanically weaker linkers (more active mechanophores) are incorporated into the middle of elastically effective strands (Figure 7a).[98] However, the weaker linkers work to strengthen elastic networks if they function as the bridge between elastically effective chains (Figure 7b).[100] By elaborately designing a network structure with mechanophores, the mechanical properties of elastic materials can be significantly altered.

A few examples of studies have successfully reduced the activation threshold strain by focusing on the micro- and macroscopic material design. Boydston and Boechler prepared SP-containing polycaprolactone and PDMS with periodic microstructures via three-dimensional printing and mold casting, respectively. The microstructured materials undergo activation at much lower global strains due to stress localization in the thin regions. A smaller microporous architecture in PDMS reduces the critical stress and strain for mechanochromic

https://doi.org/10.1021/acs.macromol.3c01280
Macromolecules 2024, 57, 425−433

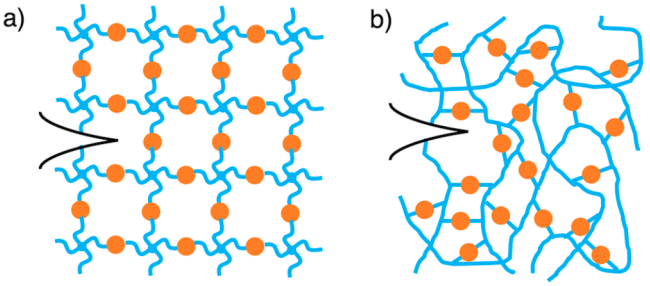


Figure 7. Polymer networks with mechanophores (a) embedded in the middle of elastically effective chains or (b) as a bridge between elastically effective chains. The orange part indicates the mechanophore.

response.[101] A 5−25 μm size pore was introduced by curing PDMS with SP and silica nanoparticles in ethanol−water hydrophilic cosolvents. Because of the stress−concentration at the interface, i.e., the pore surface, the porous PDMS composites show color change at a strain half of that of the nonporous one. The study also revealed that the critical strain gets smaller following the decrease in the pore size, while the intensity of mechanochromism and stretchability increase.

Although approaches to decrease the molecular force threshold on the basis of a mechanophore design, which avoids relying on covalent bond scissions,[72,102−107] are beyond the scope of this Perspective, a multiscale design of mechanoresponsive polymers in terms of the mechanophore, polymer structure, and material shape will pave the way for novel functions and future applications.

5. CONCLUSIONS

The paradigm shift in polymer mechanochemistry resulting from the introduction of the mechanophore concept has induced considerable progress in the development of functional polymers. The fundamental characteristics of mechanophores have been mainly investigated by ultrasonicating dilute polymer solutions, which ensures high reaction efficiency and analytical accessibility. However, despite the experimental evidence supporting the numerous potential applications of mechanophores, the low reaction efficiency in bulk systems hinders the development of practical applications. The studies mentioned in this Perspective provide insights into the design of materials with high mechanosensitivity. The establishment of strategies to improve the mechanophore response will undoubtedly be key to broadening potential applications by realizing novel functionalities such as stress strengthening and reducing the synthetic cost, which is proportional to the amount of installed mechanophores. In addition, the ability to freely control the mechanical sensitivity and response efficiency will lead to materials that can potentially identify the type[108] and magnitude[15,75,91] of the force. Taking advantage of the flexibility in designing mechanophore-based materials, it is feasible to expect that a rational macromolecular design will lead to significant breakthroughs in the field of mechanofunctional polymers in the near future.

AUTHOR INFORMATION

Corresponding Author

Hideyuki Otsuka − *Department of Chemical Science and Engineering, Tokyo Institute of Technology, Tokyo 152-8550, Japan; Living Systems Materialogy (LiSM) Research Group, International Research Frontiers Initiative (IRFI), Tokyo Institute of Technology, Yokohama 226-8501, Japan;* orcid.org/0000-0002-1512-671X; Email: otsuka@mac.titech.ac.jp

Author

Takuma Watabe − *Department of Chemical Science and Engineering, Tokyo Institute of Technology, Tokyo 152-8550, Japan*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.macromol.3c01280

Notes

The authors declare no competing financial interest.

Biographies

Takuma Watabe received his Bachelor's Degree in Engineering from Tokyo Institute of Technology, Tokyo, Japan, in 2018. He then continued his studies to obtain his Master's Degree in Engineering and graduated in 2020. Afterward, he received his Ph.D. under the supervision of Prof. Hideyuki Otsuka at Tokyo Institute of Technology in 2023 related to mechanofunctional polymer materials. He received the JSPS Research Fellowships for Young Scientists from 2020 to 2023. He began his career at a chemical manufacturer in 2023.

Hideyuki Otsuka received his Ph.D. in 1996 under the supervision of Prof. Seiji Shinkai at Kyushu University, Japan. He then moved to the University of Birmingham, UK, as a postdoctoral fellow. In 1997, he was appointed Assistant Professor in the group of Prof. Takeshi Endo at Tokyo Institute of Technology, Japan, where he started his academic research on polymer chemistry. In 2000, he was promoted to Associate Professor in the group of Prof. Atsushi Takahara at Kyushu University, Japan. In 2013, he moved to Tokyo Institute of Technology as a Full Professor. His work has been recognized by several awards such as the SPSJ (the Society of Polymer Science, Japan) Wiley Award in 2012 and

https://doi.org/10.1021/acs.macromol.3c01280
Macromolecules 2024, 57, 425−433

the CSJ (Chemical Society of Japan) Academic Award in 2021. He has published more than 280 research and review articles as well as book chapters. His current research interests are focused on polymer reactions, dynamic covalent chemistry, self-healing polymers, and polymer mechanochemistry.

■ ACKNOWLEDGMENTS

This work was supported by JST CREST Grant JPMJCR1991 (Japan).

■ REFERENCES

(1) Beyer, M. K.; Clausen-Schaumann, H. Mechanochemistry: The Mechanical Activation of Covalent Bonds. *Chem. Rev.* **2005**, *105* (8), 2921−2948.
(2) Creton, C. 50th Anniversary Perspective: Networks and Gels: Soft but Dynamic and Tough. *Macromolecules* **2017**, *50* (21), 8297−8316.
(3) Danielsen, S. P. O.; Beech, H. K.; Wang, S.; El-Zaatari, B. M.; Wang, X.; Sapir, L.; Ouchi, T.; Wang, Z.; Johnson, P. N.; Hu, Y.; et al. Molecular Characterization of Polymer Networks. *Chem. Rev.* **2021**, *121* (8), 5042−5092.
(4) Potisek, S. L.; Davis, D. A.; Sottos, N. R.; White, S. R.; Moore, J. S. Mechanophore-Linked Addition Polymers. *J. Am. Chem. Soc.* **2007**, *129* (45), 13808−13809.
(5) Davis, D. A.; Hamilton, A.; Yang, J.; Cremar, L. D.; Van Gough, D.; Potisek, S. L.; Ong, M. T.; Braun, P. V.; Martínez, T. J.; White, S. R.; et al. Force-Induced Activation of Covalent Bonds in Mechanoresponsive Polymeric Materials. *Nature* **2009**, *459* (7243), 68−72.
(6) Qiu, W.; Scofield, J. M. P.; Gurr, P. A.; Qiao, G. G. Mechanochromophore-Linked Polymeric Materials with Visible Color Changes. *Macromol. Rapid Commun.* **2022**, *43* (10), 2100866.
(7) Qian, H.; Purwanto, N. S.; Ivanoff, D. G.; Halmes, A. J.; Sottos, N. R.; Moore, J. S. Fast, Reversible Mechanochromism of Regioisomeric Oxazine Mechanophores: Developing in Situ Responsive Force Probes for Polymeric Materials. *Chem.* **2021**, *7* (4), 1080−1091.
(8) Baumann, C.; Stratigaki, M.; Centeno, S. P.; Göstl, R. Multicolor Mechanofluorophores for the Quantitative Detection of Covalent Bond Scission in Polymers. *Angew. Chem., Int. Ed.* **2021**, *60* (24), 13287−13293.
(9) Zhang, H.; Gao, F.; Cao, X.; Li, Y.; Xu, Y.; Weng, W.; Boulatov, R. Mechanochromism and Mechanical-Force-Triggered Cross-Linking from a Single Reactive Moiety Incorporated into Polymer Chains. *Angew. Chem., Int. Ed.* **2016**, *55* (9), 3040−3044.
(10) Chen, Y.; Spiering, A. J. H.; Karthikeyan, S.; Peters, G. W. M.; Meijer, E. W.; Sijbesma, R. P. Mechanically Induced Chemiluminescence from Polymers Incorporating a 1,2-Dioxetane Unit in the Main Chain. *Nat. Chem.* **2012**, *4* (7), 559−562.
(11) Imato, K.; Irie, A.; Kosuge, T.; Ohishi, T.; Nishihara, M.; Takahara, A.; Otsuka, H. Mechanophores with a Reversible Radical System and Freezing-Induced Mechanochemistry in Polymer Solutions and Gels. *Angew. Chem., Int. Ed.* **2015**, *54* (21), 6168−6172.
(12) Ishizuki, K.; Oka, H.; Aoki, D.; Goseki, R.; Otsuka, H. Mechanochromic Polymers That Turn Green Upon the Dissociation of Diarylbibenzothiophenonyl: The Missing Piece toward Rainbow Mechanochromism. *Chem.—Eur. J.* **2018**, *24* (13), 3170−3173.
(13) Sumi, T.; Goseki, R.; Otsuka, H. Tetraarylsuccinonitriles as Mechanochromophores to Generate Highly Stable Luminescent Carbon-Centered Radicals. *Chem. Commun.* **2017**, *53* (87), 11885−11888.
(14) Sakai, H.; Sumi, T.; Aoki, D.; Goseki, R.; Otsuka, H. Thermally Stable Radical-Type Mechanochromic Polymers Based on Difluorenylsuccinonitrile. *ACS Macro Lett.* **2018**, *7* (11), 1359−1363.
(15) McFadden, M. E.; Robb, M. J. Force-Dependent Multicolor Mechanochromism from a Single Mechanophore. *J. Am. Chem. Soc.* **2019**, *141* (29), 11388−11392.
(16) Qi, Q.; Sekhon, G.; Chandradat, R.; Ofodum, N. M.; Shen, T.; Scrimgeour, J.; Joy, M.; Wriedt, M.; Jayathirtha, M.; Darie, C. C.; et al. Force-Induced Near-Infrared Chromism of Mechanophore-Linked Polymers. *J. Am. Chem. Soc.* **2021**, *143* (42), 17337−17343.
(17) Huo, S.; Zhao, P.; Shi, Z.; Zou, M.; Yang, X.; Warszawik, E.; Loznik, M.; Göstl, R.; Herrmann, A. Mechanochemical Bond Scission for the Activation of Drugs. *Nat. Chem.* **2021**, *13* (2), 131−139.
(18) Shi, Z.; Song, Q.; Göstl, R.; Herrmann, A. Mechanochemical Activation of Disulfide-Based Multifunctional Polymers for Theranostic Drug Release. *Chem. Sci.* **2021**, *12* (5), 1668−1674.
(19) Küng, R.; Pausch, T.; Rasch, D.; Göstl, R.; Schmidt, B. M. Mechanochemical Release of Non-Covalently Bound Guests from a Polymer-Decorated Supramolecular Cage. *Angew. Chem., Int. Ed.* **2021**, *60* (24), 13626−13630.
(20) Sun, Y.; Neary, W. J.; Burke, Z. P.; Qian, H.; Zhu, L.; Moore, J. S. Mechanically Triggered Carbon Monoxide Release with Turn-On Aggregation-Induced Emission. *J. Am. Chem. Soc.* **2022**, *144* (3), 1125−1129.
(21) Lu, Y.; Sugita, H.; Mikami, K.; Aoki, D.; Otsuka, H. Mechanochemical Reactions of Bis(9-Methylphenyl-9-Fluorenyl) Peroxides and Their Applications in Cross-Linked Polymers. *J. Am. Chem. Soc.* **2021**, *143* (42), 17744−17750.
(22) Hu, X.; Zeng, T.; Husic, C. C.; Robb, M. J. Mechanically Triggered Small Molecule Release from a Masked Furfuryl Carbonate. *J. Am. Chem. Soc.* **2019**, *141* (38), 15018−15023.
(23) Piermattei, A.; Karthikeyan, S.; Sijbesma, R. P. Activating Catalysts with Mechanical Force. *Nat. Chem.* **2009**, *1* (2), 133−137.
(24) Versaw, B. A.; Zeng, T.; Hu, X.; Robb, M. J. Harnessing the Power of Force: Development of Mechanophores for Molecular Release. *J. Am. Chem. Soc.* **2021**, *143* (51), 21461−21473.
(25) Küng, R.; Göstl, R.; Schmidt, B. M. Release of Molecular Cargo from Polymer Systems by Mechanochemistry. *Chem.—Eur. J.* **2022**, *28* (17), No. e202103860.
(26) Clough, J. M.; Balan, A.; Van Daal, T. L. J.; Sijbesma, R. P. Probing Force with Mechanobase-Induced Chemiluminescence. *Angew. Chem., Int. Ed.* **2016**, *55* (4), 1445−1449.
(27) Jakobs, R. T. M.; Ma, S.; Sijbesma, R. P. Mechanocatalytic Polymerization and Cross-Linking in a Polymeric Matrix. *ACS Macro Lett.* **2013**, *2* (7), 613−616.
(28) Wang, Z.; Zheng, X.; Ouchi, T.; Kouznetsova, T. B.; Beech, H. K.; Av-Ron, S.; Matsuda, T.; Bowser, B. H.; Wang, S.; Johnson, J. A.; et al. Toughening Hydrogels through Force-Triggered Chemical Reactions That Lengthen Polymer Strands. *Science* **2021**, *374* (6564), 193−196.
(29) Diesendruck, C. E.; Peterson, G. I.; Kulik, H. J.; Kaitz, J. A.; Mar, B. D.; May, P. A.; White, S. R.; Martínez, T. J.; Boydston, A. J.; Moore, J. S. Mechanically Triggered Heterolytic Unzipping of a Low-Ceiling-Temperature Polymer. *Nat. Chem.* **2014**, *6* (7), 623−628.
(30) Yang, J.; Xia, Y. Mechanochemical Generation of Acid-Degradable Poly(Enol Ether)S. *Chem. Sci.* **2021**, *12* (12), 4389−4394.
(31) Hsu, T. G.; Zhou, J.; Su, H. W.; Schrage, B. R.; Ziegler, C. J.; Wang, J. A Polymer with "Locked" Degradability: Superior Backbone Stability and Accessible Degradability Enabled by Mechanophore Installation. *J. Am. Chem. Soc.* **2020**, *142* (5), 2100−2104.
(32) Lin, Y.; Kouznetsova, T. B.; Craig, S. L. Mechanically Gated Degradable Polymers. *J. Am. Chem. Soc.* **2020**, *142* (5), 2105−2109.
(33) Ramirez, A. L. B.; Kean, Z. S.; Orlicki, J. A.; Champhekar, M.; Elsakr, S. M.; Krause, W. E.; Craig, S. L. Mechanochemical Strengthening of a Synthetic Polymer in Response to Typically Destructive Shear Forces. *Nat. Chem.* **2013**, *5* (9), 757−761.
(34) Seshimo, K.; Sakai, H.; Watabe, T.; Aoki, D.; Sugita, H.; Mikami, K.; Mao, Y.; Ishigami, A.; Nishitsuji, S.; Kurose, T.; et al. Segmented Polyurethane Elastomers with Mechanochromic and Self-Strengthening Functions. *Angew. Chem., Int. Ed.* **2021**, *60* (15), 8406−8409.
(35) Verstraeten, F.; Göstl, R.; Sijbesma, R. P. Stress-Induced Colouration and Crosslinking of Polymeric Materials by Mechanochemical Formation of Triphenylimidazolyl Radicals. *Chem. Commun.* **2016**, *52* (55), 8608−8611.
(36) Wang, J.; Piskun, I.; Craig, S. L. Mechanochemical Strengthening of a Multi-Mechanophore Benzocyclobutene Polymer. *ACS Macro Lett.* **2015**, *4* (8), 834−837.

https://doi.org/10.1021/acs.macromol.3c01280
Macromolecules 2024, 57, 425−433

(37) Hickenboth, C. R.; Moore, J. S.; White, S. R.; Sottos, N. R.; Baudry, J.; Wilson, S. R. Biasing Reaction Pathways with Mechanical Force. *Nature* **2007**, *446* (7134), 423−427.
(38) Lenhardt, J. M.; Ong, M. T.; Choe, R.; Evenhuis, C. R.; Martinez, T. J.; Craig, S. L. Trapping a Diradical Transition State by Mechanochemical Polymer Extension. *Science* **2010**, *329* (5995), 1057−1060.
(39) Chen, Z.; Mercer, J. A. M.; Zhu, X.; Romaniuk, J. A. H.; Pfattner, R.; Cegelski, L.; Martinez, T. J.; Burns, N. Z.; Xia, Y. Mechanochemical Unzipping of Insulating Polyladderene to Semiconducting Polyacetylene. *Science* **2017**, *357* (6350), 475−479.
(40) Boswell, B. R.; Mansson, C. M. F.; Cox, J. M.; Jin, Z.; Romaniuk, J. A. H.; Lindquist, K. P.; Cegelski, L.; Xia, Y.; Lopez, S. A.; Burns, N. Z. Mechanochemical Synthesis of an Elusive Fluorinated Polyacetylene. *Nat. Chem.* **2021**, *13* (1), 41−46.
(41) Yang, J.; Horst, M.; Werby, S. H.; Cegelski, L.; Burns, N. Z.; Xia, Y. Bicyclohexene-Peri-Naphthalenes: Scalable Synthesis, Diverse Functionalization, Efficient Polymerization, and Facile Mechanoactivation of Their Polymers. *J. Am. Chem. Soc.* **2020**, *142* (34), 14619−14626.
(42) Chen, Y.; Mellot, G.; Van Luijk, D.; Creton, C.; Sijbesma, R. P. Mechanochemical Tools for Polymer Materials. *Chem. Soc. Rev.* **2021**, *50* (6), 4100−4140.
(43) Li, M.; Zhang, Q.; Zhou, Y. N.; Zhu, S. Let Spiropyran Help Polymers Feel Force! *Prog. Polym. Sci.* **2018**, *79*, 26−39.
(44) Ghanem, M. A.; Basu, A.; Behrou, R.; Boechler, N.; Boydston, A. J.; Craig, S. L.; Lin, Y.; Lynde, B. E.; Nelson, A.; Shen, H.; et al. The Role of Polymer Mechanochemistry in Responsive Materials and Additive Manufacturing. *Nat. Rev. Mater.* **2021**, *6* (1), 84−98.
(45) Lloyd, E. M.; Vakil, J. R.; Yao, Y.; Sottos, N. R.; Craig, S. L. Covalent Mechanochemistry and Contemporary Polymer Network Chemistry: A Marriage in the Making. *J. Am. Chem. Soc.* **2023**, *145* (2), 751−768.
(46) Matsuda, T.; Kawakami, R.; Namba, R.; Nakajima, T.; Gong, J. P. Mechanoresponsive Self-Growing Hydrogels Inspired by Muscle Training. *Science* **2019**, *363* (6426), 504−508.
(47) Stevenson, R.; De Bo, G. Controlling Reactivity by Geometry in Retro-Diels-Alder Reactions under Tension. *J. Am. Chem. Soc.* **2017**, *139* (46), 16768−16771.
(48) Kryger, M. J.; Munaretto, A. M.; Moore, J. S. Structure-Mechanochemical Activity Relationships for Cyclobutane Mechanophores. *J. Am. Chem. Soc.* **2011**, *133* (46), 18992−18998.
(49) Wang, F.; Diesendruck, C. E. Effect of Disulphide Loop Length on Mechanochemical Structural Stability of Macromolecules. *Chem. Commun.* **2020**, *56* (14), 2143−2146.
(50) Lin, Y.; Barbee, M. H.; Chang, C. C.; Craig, S. L. Regiochemical Effects on Mechanophore Activation in Bulk Materials. *J. Am. Chem. Soc.* **2018**, *140* (46), 15969−15975.
(51) Gossweiler, G. R.; Kouznetsova, T. B.; Craig, S. L. Force-Rate Characterization of Two Spiropyran-Based Molecular Force Probes. *J. Am. Chem. Soc.* **2015**, *137* (19), 6148−6151.
(52) Robb, M. J.; Kim, T. A.; Halmes, A. J.; White, S. R.; Sottos, N. R.; Moore, J. S. Regioisomer-Specific Mechanochromism of Naphthopyran in Polymeric Materials. *J. Am. Chem. Soc.* **2016**, *138* (38), 12328−12331.
(53) May, P. A.; Moore, J. S. Polymer Mechanochemistry: Techniques to Generate Molecular Force via Elongational Flows. *Chem. Soc. Rev.* **2013**, *42* (18), 7497−7506.
(54) May, P. A.; Munaretto, N. F.; Hamoy, M. B.; Robb, M. J.; Moore, J. S. Is Molecular Weight or Degree of Polymerization a Better Descriptor of Ultrasound-Induced Mechanochemical Transduction? *ACS Macro Lett.* **2016**, *5* (2), 177−180.
(55) Church, D. C.; Peterson, G. I.; Boydston, A. J. Comparison of Mechanochemical Chain Scission Rates for Linear versus Three-Arm Star Polymers in Strong Acoustic Fields. *ACS Macro Lett.* **2014**, *3* (7), 648−651.
(56) Oka, H.; Imato, K.; Sato, T.; Ohishi, T.; Goseki, R.; Otsuka, H. Enhancing Mechanochemical Activation in the Bulk State by Designing Polymer Architectures. *ACS Macro Lett.* **2016**, *5* (10), 1124−1127.
(57) Bowser, B. H.; Craig, S. L. Empowering Mechanochemistry with Multi-Mechanophore Polymer Architectures. *Polym. Chem.* **2018**, *9* (26), 3583−3593.
(58) Pan, Y.; Zhang, H.; Xu, P.; Tian, Y.; Wang, C.; Xiang, S.; Boulatov, R.; Weng, W. A Mechanochemical Reaction Cascade for Controlling Load-Strengthening of a Mechanochromic Polymer. *Angew. Chem., Int. Ed.* **2020**, *59* (49), 21980−21985.
(59) Li, H.; Göstl, R.; Delgove, M.; Sweeck, J.; Zhang, Q.; Sijbesma, R. P.; Heuts, J. P. A. Promoting Mechanochemistry of Covalent Bonds by Noncovalent Micellar Aggregation. *ACS Macro Lett.* **2016**, *5* (9), 995−998.
(60) Izak-Nau, E.; Braun, S.; Pich, A.; Göstl, R. Mechanically Resistant Poly(N-Vinylcaprolactam) Microgels with Sacrificial Supramolecular Catechin Hydrogen Bonds. *Adv. Sci.* **2022**, *9* (12), 1−8.
(61) Kharandiuk, T.; Tan, K. H.; Xu, W.; Weitenhagen, F.; Braun, S.; Göstl, R.; Pich, A. Mechanoresponsive Diselenide-Crosslinked Microgels with Programmed Ultrasound-Triggered Degradation and Radical Scavenging Ability for Protein Protection. *Chem. Sci.* **2022**, *13* (38), 11304−11311.
(62) Peterson, G. I.; Bang, K. T.; Choi, T. L. Mechanochemical Degradation of Denpols: Synthesis and Ultrasound-Induced Chain Scission of Polyphenylene-Based Dendronized Polymers. *J. Am. Chem. Soc.* **2018**, *140* (27), 8599−8608.
(63) Noh, J.; Peterson, G. I.; Choi, T. L. Mechanochemical Reactivity of Bottlebrush and Dendronized Polymers: Solid vs. Solution States. *Angew. Chem., Int. Ed.* **2021**, *60* (34), 18651−18659.
(64) Peterson, G. I.; Ko, W.; Hwang, Y. J.; Choi, T. L. Mechanochemical Degradation of Amorphous Polymers with Ball-Mill Grinding: Influence of the Glass Transition Temperature. *Macromolecules* **2020**, *53* (18), 7795−7802.
(65) Peterson, G. I.; Choi, T. L. The Influence of Polymer Architecture in Polymer Mechanochemistry. *Chem. Commun.* **2021**, *57* (53), 6465−6474.
(66) Jiang, S.; Zhang, L.; Xie, T.; Lin, Y.; Zhang, H.; Xu, Y.; Weng, W.; Dai, L. Mechanoresponsive PS-PnBA-PS Triblock Copolymers via Covalently Embedding Mechanophore. *ACS Macro Lett.* **2013**, *2* (8), 705−709.
(67) Chen, Y.; Zhang, H.; Fang, X.; Lin, Y.; Xu, Y.; Weng, W. Mechanical Activation of Mechanophore Enhanced by Strong Hydrogen Bonding Interactions. *ACS Macro Lett.* **2014**, *3* (2), 141−145.
(68) Fang, X.; Zhang, H.; Chen, Y.; Lin, Y.; Xu, Y.; Weng, W. Biomimetic Modular Polymer with Tough and Stress Sensing Properties. *Macromolecules* **2013**, *46* (16), 6566−6574.
(69) Chen, Y.; Sijbesma, R. P. Dioxetanes as Mechanoluminescent Probes in Thermoplastic Elastomers. *Macromolecules* **2014**, *47* (12), 3797−3805.
(70) Li, X.; Li, J.; Wei, W.; Yang, F.; Wu, M.; Wu, Q.; Xie, T.; Chen, Y. Enhanced Mechanochemiluminescence from End-Functionalized Polyurethanes with Multiple Hydrogen Bonds. *Macromolecules* **2021**, *54* (3), 1557−1563.
(71) Michael, P.; Biewend, M.; Binder, W. H. Mechanochemical Activation of Fluorogenic CuAAC "Click" Reactions for Stress-Sensing Applications. *Macromol. Rapid Commun.* **2018**, *39* (22), 1800376.
(72) Kotani, R.; Yokoyama, S.; Nobusue, S.; Yamaguchi, S.; Osuka, A.; Yabu, H.; Saito, S. Bridging Pico-to-Nanonewtons with a Ratiometric Force Probe for Monitoring Nanoscale Polymer Physics before Damage. *Nat. Commun.* **2022**, *13* (1), 303.
(73) Ouchi, T.; Wang, W.; Silverstein, B. E.; Johnson, J. A.; Craig, S. L. Effect of Strand Molecular Length on Mechanochemical Transduction in Elastomers Probed with Uniform Force Sensors. *Polym. Chem.* **2023**, *14* (14), 1646−1655.
(74) Kosuge, T.; Imato, K.; Goseki, R.; Otsuka, H. Polymer-Inorganic Composites with Dynamic Covalent Mechanochromophore. *Macromolecules* **2016**, *49* (16), 5903−5911.
(75) Kosuge, T.; Zhu, X.; Lau, V. M.; Aoki, D.; Martinez, T. J.; Moore, J. S.; Otsuka, H. Multicolor Mechanochromism of a Polymer/Silica Composite with Dual Distinct Mechanophores. *J. Am. Chem. Soc.* **2019**, *141* (5), 1898−1902.

https://doi.org/10.1021/acs.macromol.3c01280
Macromolecules 2024, 57, 425−433

(76) Kim, T. A.; Lamuta, C.; Kim, H.; Leal, C.; Sottos, N. R. Interfacial Force-Focusing Effect in Mechanophore-Linked Nanocomposites. *Adv. Sci.* **2020**, *7* (7), 1903464.
(77) Nakajima, K.; Watabe, H.; Nishi, T. Single Polymer Chain Rubber Elasticity Investigated by Atomic Force Microscopy. *Polymer* **2006**, *47* (7), 2505−2510.
(78) Yao, R.; Li, X.; Xiao, N.; Weng, W.; Zhang, W. Single-Molecule Observation of Mechanical Isomerization of Spirothiopyran and Subsequent Click Addition. *Nano Res.* **2021**, *14* (8), 2654−2658.
(79) Barbee, M. H.; Kouznetsova, T.; Barrett, S. L.; Gossweiler, G. R.; Lin, Y.; Rastogi, S. K.; Brittain, W. J.; Craig, S. L. Substituent Effects and Mechanism in a Mechanochemical Reaction. *J. Am. Chem. Soc.* **2018**, *140* (40), 12746−12750.
(80) Gu, Y.; Zhao, J.; Johnson, J. A. Polymer Networks: From Plastics and Gels to Porous Frameworks. *Angew. Chem., Int. Ed.* **2020**, *59* (13), 5022−5049.
(81) Vernerey, F. J.; Brighenti, R.; Long, R.; Shen, T. Statistical Damage Mechanics of Polymer Networks. *Macromolecules* **2018**, *51* (17), 6609−6622.
(82) Sakai, H.; Aoki, D.; Seshimo, K.; Mayumi, K.; Nishitsuji, S.; Kurose, T.; Ito, H.; Otsuka, H. Visualization and Quantitative Evaluation of Toughening Polymer Networks by a Sacrificial Dynamic Cross-Linker with Mechanochromic Properties. *ACS Macro Lett.* **2020**, *9* (8), 1108−1113.
(83) Yang, L.; Ouyang, P.; Chen, Y.; Xiang, S.; Ruan, Y.; Weng, W.; He, X.; Xia, H. Tough Self-Reporting Elastomer with NIR Induced Shape Memory Effect. *Giant* **2021**, *8*, 100069.
(84) Clough, J. M.; Creton, C.; Craig, S. L.; Sijbesma, R. P. Covalent Bond Scission in the Mullins Effect of a Filled Elastomer: Real-Time Visualization with Mechanoluminescence. *Adv. Funct. Mater.* **2016**, *26* (48), 9063−9074.
(85) Raisch, M.; Genovese, D.; Zaccheroni, N.; Schmidt, S. B.; Focarete, M. L.; Sommer, M.; Gualandi, C. Highly Sensitive, Anisotropic, and Reversible Stress/Strain-Sensors from Mechanochromic Nanofiber Composites. *Adv. Mater.* **2018**, *30* (39), 1802813.
(86) Beiermann, B. A.; Kramer, S. L. B.; Moore, J. S.; White, S. R.; Sottos, N. R. Role of Mechanophore Orientation in Mechanochemical Reactions. *ACS Macro Lett.* **2012**, *1* (1), 163−166.
(87) Qiu, W.; Gurr, P. A.; Qiao, G. G. Regulating Color Activation Energy of Mechanophore-Linked Multinetwork Elastomers. *Macromolecules* **2020**, *53* (10), 4090−4098.
(88) Watabe, T.; Aoki, D.; Otsuka, H. Polymer-Network Toughening and Highly Sensitive Mechanochromism via a Dynamic Covalent Mechanophore and a Multinetwork Strategy. *Macromolecules* **2022**, *55* (13), 5795−5802.
(89) Nakajima, T. Generalization of the Sacrificial Bond Principle for Gel and Elastomer Toughening. *Polym. J.* **2017**, *49* (6), 477−485.
(90) Watabe, T.; Otsuka, H. Swelling-Induced Mechanochromism in Multinetwork Polymers. *Angew. Chem., Int. Ed.* **2023**, *62* (9), No. e202216469.
(91) Wang, T.; Wang, H.; Shen, L.; Zhang, N. Multicolor Mechanochromism of a Multinetwork Elastomer That Can Distinguish between Low and High Stress. *Polym. Chem.* **2021**, *12* (26), 3832−3841.
(92) Chen, Y.; Yeh, C. J.; Guo, Q.; Qi, Y.; Long, R.; Creton, C. Fast Reversible Isomerization of Merocyanine as a Tool to Quantify Stress History in Elastomers. *Chem. Sci.* **2021**, *12* (5), 1693−1701.
(93) Ducrot, E.; Chen, Y.; Bulters, M.; Sijbesma, R. P.; Creton, C. Toughening Elastomers with Sacrificial Bonds and Watching Them Break. *Science* **2014**, *344* (6180), 186−189.
(94) Wang, T.; Zhang, N.; Dai, J.; Li, Z.; Bai, W.; Bai, R. Novel Reversible Mechanochromic Elastomer with High Sensitivity: Bond Scission and Bending-Induced Multicolor Switching. *ACS Appl. Mater. Interfaces* **2017**, *9* (13), 11874−11881.
(95) Zhang, H.; Zeng, D.; Pan, Y.; Chen, Y.; Ruan, Y.; Xu, Y.; Boulatov, R.; Creton, C.; Weng, W. Mechanochromism and Optical Remodeling of Multi-Network Elastomers Containing Anthracene Dimers. *Chem. Sci.* **2019**, *10* (36), 8367−8373.
(96) Chen, Y.; Yeh, C. J.; Qi, Y.; Long, R.; Creton, C. From Force-Responsive Molecules to Quantifying and Mapping Stresses in Soft Materials. *Sci. Adv.* **2020**, *6* (20), No. eaaz5093.
(97) Kim, D. W.; Medvedev, G. A.; Caruthers, J. M.; Jo, J. Y.; Won, Y. Y.; Kim, J. Enhancement of Mechano-Sensitivity for Spiropyran-Linked Poly(Dimethylsiloxane) via Solvent Swelling. *Macromolecules* **2020**, *53* (18), 7954−7961.
(98) Wang, S.; Beech, H. K.; Bowser, B. H.; Kouznetsova, T. B.; Olsen, B. D.; Rubinstein, M.; Craig, S. L. Mechanism Dictates Mechanics: A Molecular Substituent Effect in the Macroscopic Fracture of a Covalent Polymer Network. *J. Am. Chem. Soc.* **2021**, *143* (10), 3714−3718.
(99) Wang, Z.; Zheng, X.; Ouchi, T.; Kouznetsova, T. B.; Beech, H. K.; Av-Ron, S.; Matsuda, T.; Bowser, B. H.; Wang, S.; Johnson, J. A.; et al. Toughening Hydrogels through Force-Triggered Chemical Reactions That Lengthen Polymer Strands. *Science* **2021**, *374* (6564), 193.
(100) Wang, S.; Hu, Y.; Kouznetsova, T. B.; Sapir, L.; Chen, D.; Herzog-Arbeitman, A.; Johnson, J. A.; Rubinstein, M.; Craig, S. L. Facile Mechanochemical Cycloreversion of Polymer Cross-Linkers Enhances Tear Resistance. *Science* **2023**, *380* (6651), 1248−1252.
(101) Park, J.; Lee, Y.; Barbee, M. H.; Cho, S.; Cho, S.; Shanker, R.; Kim, J.; Myoung, J.; Kim, M. P.; Baig, C.; Craig, S. L.; Ko, H. A Hierarchical Nanoparticle-in-Micropore Architecture for Enhanced Mechanosensitivity and Stretchability in Mechanochromic Electronic Skins. *Adv. Mater.* **2019**, *31* (25), 1808148.
(102) Hu, H.; Cheng, X.; Ma, Z.; Sijbesma, R. P.; Ma, Z. Polymer Mechanochromism from Force-Tuned Excited-State Intramolecular Proton Transfer. *J. Am. Chem. Soc.* **2022**, *144* (22), 9971−9979.
(103) Sagara, Y.; Karman, M.; Verde-Sesto, E.; Matsuo, K.; Kim, Y.; Tamaoki, N.; Weder, C. Rotaxanes as Mechanochromic Fluorescent Force Transducers in Polymers. *J. Am. Chem. Soc.* **2018**, *140* (5), 1584−1587.
(104) Sagara, Y.; Karman, M.; Seki, A.; Pannipara, M.; Tamaoki, N.; Weder, C. Rotaxane-Based Mechanophores Enable Polymers with Mechanically Switchable White Photoluminescence. *ACS Cent. Sci.* **2019**, *5* (5), 874−881.
(105) Sagara, Y.; Traeger, H.; Li, J.; Okado, Y.; Schrettl, S.; Tamaoki, N.; Weder, C. Mechanically Responsive Luminescent Polymers Based on Supramolecular Cyclophane Mechanophores. *J. Am. Chem. Soc.* **2021**, *143* (14), 5519−5525.
(106) Traeger, H.; Sagara, Y.; Kiebala, D. J.; Schrettl, S.; Weder, C. Folded Perylene Diimide Loops as Mechanoresponsive Motifs. *Angew. Chem., Int. Ed.* **2021**, *60* (29), 16191−16199.
(107) Filonenko, G. A.; Khusnutdinova, J. R. Dynamic Phosphorescent Probe for Facile and Reversible Stress Sensing. *Adv. Mater.* **2017**, *29* (22), 1700563.
(108) Ishizuki, K.; Aoki, D.; Goseki, R.; Otsuka, H. Multicolor Mechanochromic Polymer Blends That Can Discriminate between Stretching and Grinding. *ACS Macro Lett.* **2018**, *7* (5), 556−560.

https://doi.org/10.1021/acs.macromol.3c01280
Macromolecules 2024, 57, 425−433