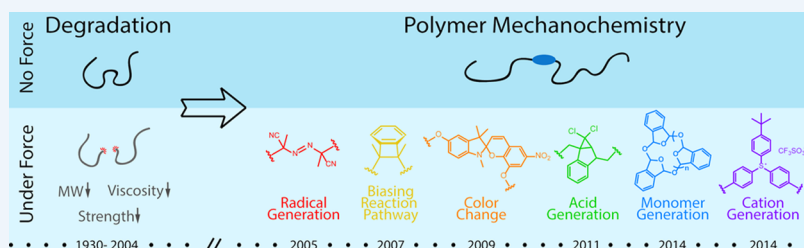# Polymer Mechanochemistry: From Destructive to Productive

Jun Li, Chikkannagari Nagamani, and Jeffrey S. Moore*

Beckman Institute for Advanced Science and Technology, Department of Materials Science and Engineering, Department of Chemistry, University of Illinois at Urbana–Champaign, Urbana, Illinois 61801, United States

**CONSPECTUS:** When one brings "polymeric materials" and "mechanical action" into the same conversation, the topic of this discussion might naturally focus on everyday circumstances such as failure of fibers, fatigue of composites, abrasion of coatings, etc. This intuitive viewpoint reflects the historic consensus in both academia and industry that mechanically induced chemical changes are destructive, leading to polymer degradation that limits materials lifetime on both macroscopic and molecular levels. In the 1930s, Staudinger observed mechanical degradation of polymers, and Melville later discovered that polymer chain scission caused the degradation. Inspired by these historical observations, we sought to redirect the destructive mechanical energy to a productive form that enables mechanoresponsive functions.

In this Account, we provide a personal perspective on the origin, barriers, developments, and key advancements of polymer mechanochemistry. We revisit the seminal events that offered molecular-level insights into the mechanochemical behavior of polymers and influenced our thinking. We also highlight the milestones achieved by our group along with the contributions from key comrades at the frontier of this field. We present a workflow for the design, evaluation, and development of new "mechanophores", a term that has come to mean a molecular unit that chemically responds in a selective manner to a mechanical perturbation. We discuss the significance of computation in identifying pairs of points on the mechanophore that promote stretch-induced activation. Attaching polymer chains to the mechanophore at the most sensitive pair and locating the mechanophore near the center of a linear polymer are thought to maximize the efficiency of mechanical-to-chemical energy transduction. We also emphasize the importance of control experiments to validate mechanochemical transformations, both in solution and in the solid state, to differentiate "mechanical" from "thermal" activation. This Account offers our first-hand perspective of the change-in-thinking in polymer mechanochemistry from "destructive" to "productive" and looks at future advances that will stimulate this growing field.

## 1. INTRODUCTION

Polymers, owing to their unique mechanical properties such as high strength, toughness, and elasticity, together with their processability, are widely sought-after synthetic materials for a wide range of everyday applications including consumer products, packaging, coatings, medical devices, electronics, and engineering composites. Understanding the influence of external mechanical stress on the mechanical properties and stability of polymeric materials has long been an important area of study to determine their in-use performance. Stimuli-responsive polymers that elicit a desired output when subjected to a specific chemical or physical input have recently gained attention.[1-4] Polymers that change their properties upon application of external stimuli such as light,[5-7] heat,[5,8] pH,[4,8-10] or redox potential[4,11,12] are now ubiquitous. The chain-like character of polymers is well-suited to transiently accumulate mechanical energy along the backbone. This behavior and the quest for new stimuli-responsive materials have resulted in mechanoresponsive polymers that use mechanical energy to drive chemical

transformations. Not only are mechanoresponsive polymers of interest in the field of synthetic materials, but sensing and transduction of mechanical stress by the extracellular matrix of eukaryotic cells is key to several biological processes such as cell growth, activation of ion channels, enzyme catalysis, hearing, and touch sensitivity.[13-16] While there is much to learn from biology about mechanochemical transduction, this Account only covers the abiotic aspects of the topic.

The response of polymeric materials to mechanical stress may vary from simple conformational changes to bond-bending and bond-stretching deformations. With sufficient force, bond scission occurs, and mechanical properties are compromised. The molecular response of synthetic polymeric materials to applied mechanical stress was first considered by Staudinger and co-workers in the 1930s.[17-19] The involvement of homolytic scission of C–C covalent bonds along the polymer backbone
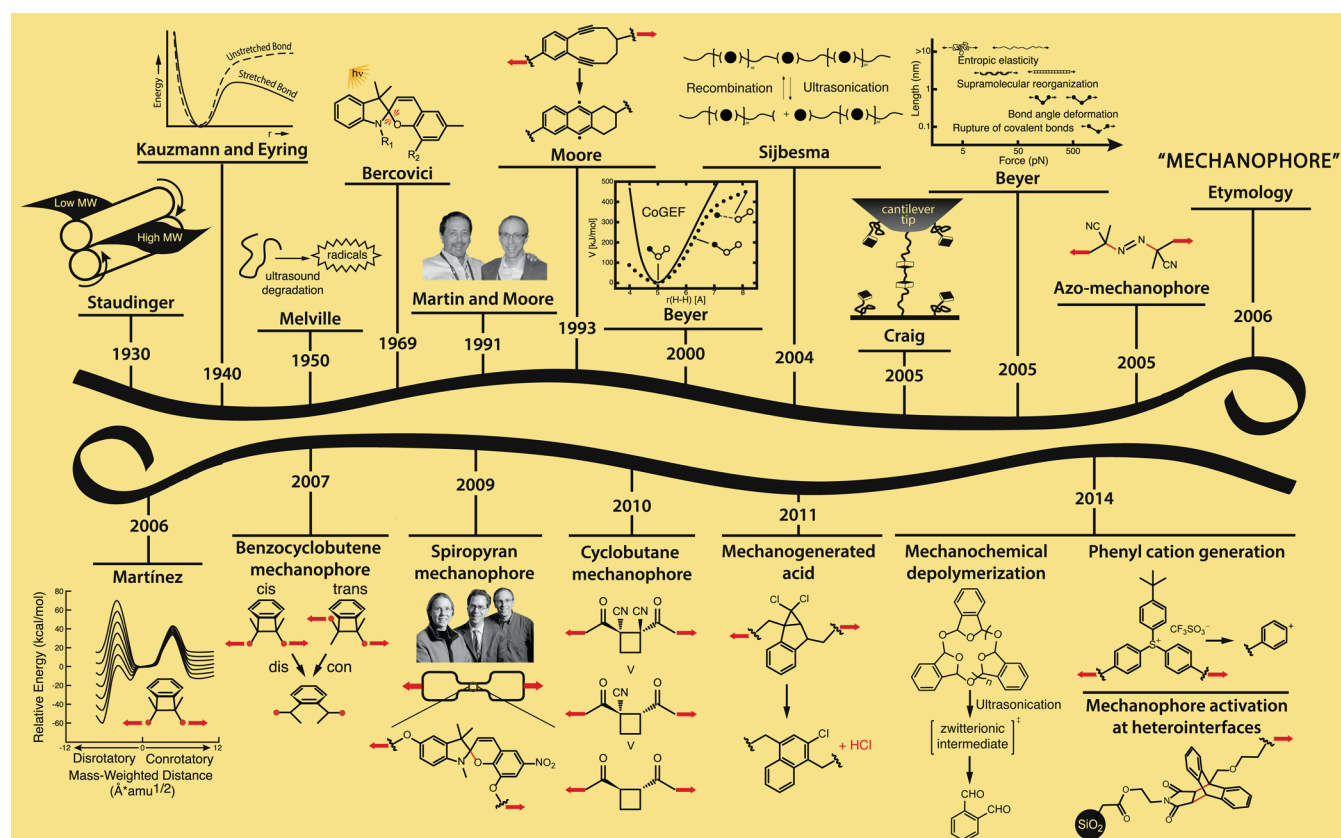
**Figure 1.** Timeline of polymer mechanochemistry developments in the Moore group, including key historical events and contributions from other researchers that influenced our thinking.

under mechanical stress was later experimentally demonstrated by Sohma et al. using electron spin resonance (ESR).[20] Early work in the field of polymer mechanochemistry was largely focused on studying the mechanochemical degradation of polymers; consequently, a bias may have developed in polymer science that mechanically induced chemical changes are associated primarily with materials degradation and mechanical failure. However, in recent years there has been a shift in the landscape of modern polymer mechanochemistry from being "destructive" to "productive", conceptualized, in part, around the idea of the "mechanophore" (Figures 1 and 2). A mechanophore is a force-sensitive molecular unit that possesses mechanically labile bonds. When incorporated within mechanically stressed polymers, mechanophores undergo chemical transformations. In 2005, our group showed that poly(ethylene glycol) function-alized with a single azo moiety at the center *selectively* cleaves at the weak azo linkage when subjected to an acoustic field generated by ultrasound (Figure 1).[21] The intentional coupling of applied mechanical forces to a reactive molecular potential energy surface so as to elicit productive chemical transformations in polymers has become a new way of thinking about polymer mechanochemistry. Mechanophore design has progressed considerably over the past few years, providing access to a wide range of desirable transformations, including color/fluorescence change,[22,23] biasing reaction pathways to access symmetry-forbidden electrocyclic ring opening reactions,[24] isomerizations,[25] releasing of small molecules,[26] generating proton catalysts,[27] and activating latent transition metal catalysts[28,29] (Figure 2).

Recent developments in the field of polymer mechanochemistry have largely focused on (i) the design and synthesis of new mechanophores for use in varied applications such as stress sensing, catalysis, self-healing, etc., and (ii) fundamental understanding of macromolecular architectures and the physical attributes of polymers that promote the efficient transduction of force into chemical change. To date, homopolymers and cross-linked polymer networks are the widely exploited architectures for mechanophore activation in solution and the solid state, respectively. Currently, our group is also investigating the activation of mechanophores at heterointerfaces.[30] Given the prevalence of composite materials in engineering and industrial applications, understanding the nature of polymer mechano-chemistry at interfaces serves to broaden the technological scope.

This Account provides a brief overview of the history of polymer mechanochemistry as well as the research efforts of the Moore group in this field. We also discuss our approach to the molecular design of mechanophores, their experimental development, the various methods of applying mechanical force to polymers, and the analytical methods to study their force-induced chemical change. For a more comprehensive coverage of the field, the reader is referred to several recent reviews.[31−34]

## 2. TIMELINE OF POLYMER MECHANOCHEMISTRY DEVELOPMENTS IN THE MOORE GROUP

### 2.1. Historical Events That Influenced Our Thinking

The early traceable demonstrations of polymer mechanochem-istry were published by Staudinger in the 1930s in which a reduction of molecular weight (MW) was observed when poly(styrene) was subjected to mastication.[17−19] Early theoreti-cal treatment of macromolecular flow by Kauzmann and Eyring for the first time quantitatively proposed that bond dissociation

## Destructive Chemistry
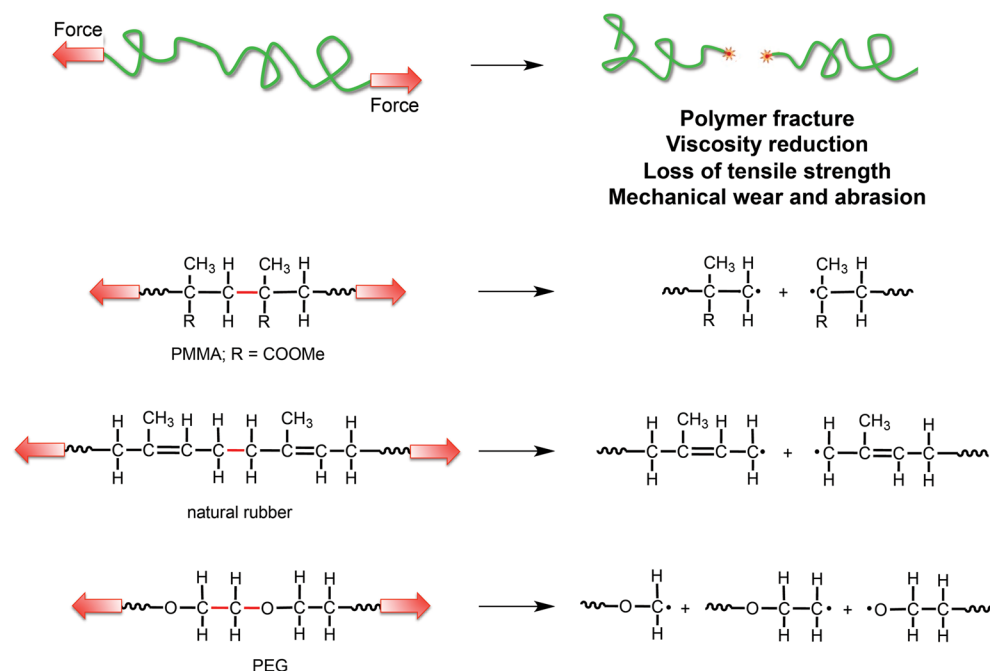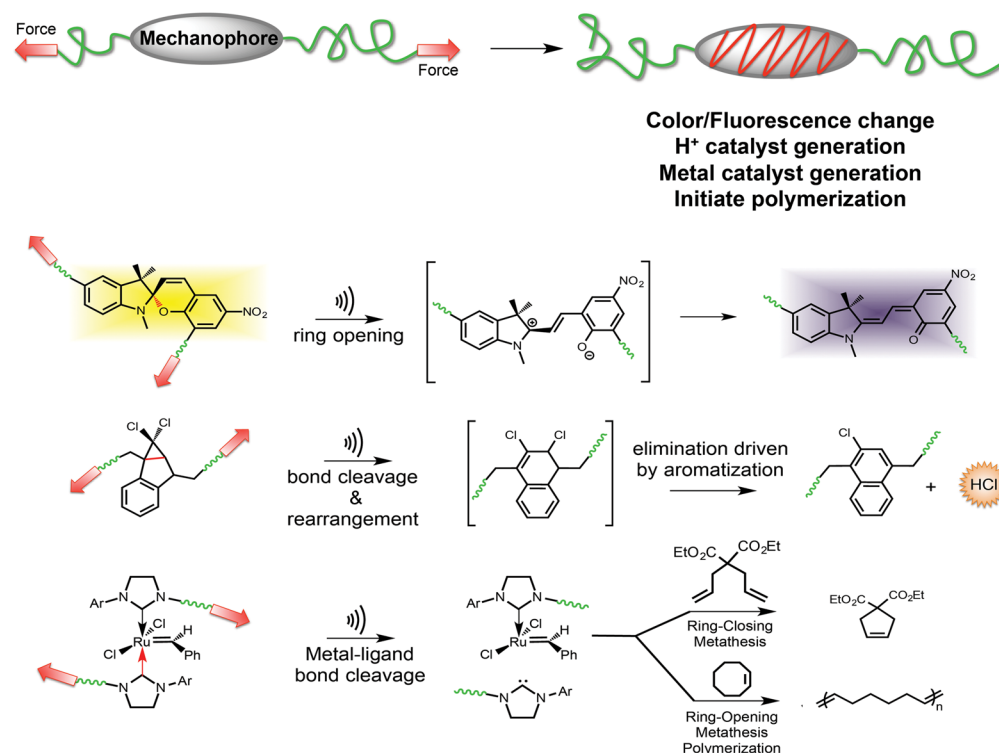


## Productive Chemistry



**Figure 2.** Change in landscape of modern polymer mechanochemistry from "destructive" to "productive" chemistry.

energy diminishes under shear force and leads to chain scission.[35] In the 1950s, Melville and Murray experimentally elucidated the nature of ultrasonic polymer degradation in solution.[36] Subjecting a poly(methacrylate) solution containing styrene to ultrasonication resulted in the initiation of polymerization

events, suggesting homolytic bond rupture and radical generation during cavitation-induced cleavage of poly-(methacrylate). Although the initiation of polymerization was indirect evidence for radical formation under ultrasonication, Melville's elegant design founded the molecular-level under-

standing of stress-induced polymer degradation. Importantly, this work stands as an early example illustrating the productive synthetic application of mechanochemical transduction. Later in the 1960s, researchers used electron spin resonance (ESR) spectroscopy to provide direct experimental evidence for the generation of free radicals from mechanical failure.[20] Elongational flow studies of dilute polymer solutions to bring about chain scission were also reported during this period.[37,38]

The Moore group took inspirations from the early explorations and began to view the nature of polymer mechanochemistry in a different way from the consensus that mechanical force is destructive. As a graduate student, one of us (J.S.M.) was familiar with research in Richard Wool's group, which demonstrated that placing isotactic polypropylene under a mechanical load led to stress-induced infrared spectral shifts.[39] In the early 1990s, conversations between J.S.M. and former colleague Prof. Dave Martin at the University of Michigan stimulated early ideas on the productive use of mechanical force in polymer chemistry. Our first proposal involved the use of strain-triggered Bergman cyclization of enediyne macrocycles to generate free radicals for initiating polymerization and cross-linking events. This idea was not carried out right away but finally witnessed its renaissance almost 10 years later.[40]

A series of advancements from which we benefited significantly are the computational techniques developed by the Beyer group in early 2000s.[41] Constrained geometries simulate external force (CoGEF) is a computational algorithm that predicts the action of molecular stretching deformations using quantum chemical calculations. This theoretical approach has enabled rational design of functional mechanophores as detailed in Section 4 (vide infra). Readdressing the model proposed by Kauzmann in 1940, Beyer and Clausen-Schaumann published an influential review on molecular mechanochemistry.[42] This review comprehensively surveyed various mechanochemical pathways of a chemical reaction as a less-known approach compared with thermo-, electro-, and photochemistry and explicitly revealed the mechanochemical nature of many chemical phenomena.

Discussions with many other colleagues in 2005 significantly influenced our pursuits in mechanochemistry. In particular, Prof. Stephen Craig described his discovery of a supramolecular polymeric network cross-linked by metal−ligand coordination and the relationship between mechanical properties and dissociation equilibrium during his visit to the UIUC campus in 2005.[43] Many conversations between J.S.M. and former colleague Prof. Todd Martínez on the force-modified potential energy surface (FMPES)[44] collectively ignited our shared interest in developing a chemistry system that selectively responds to external force perturbation. Our early sonication experiments benefited greatly from the help of colleague Prof. Ken Suslick. Collaborations with Scott White, Nancy Sottos, and Paul Braun from the University of Illinois further motivated and significantly impacted how the research unfolded. Continuous inspirations and efforts from these and other researchers for the past decade led to incredibly fruitful research findings in the development of macroscopic-force-responsive materials.

## 2.2. Etymology of "Mechanophore": From Destructive to Productive

Our group's debut of polymer mechanochemistry was the demonstration of site-specific and almost exclusive bond-specific cleavage at an azo moiety placed near the center of poly(ethylene glycol).[21] This result and the intensely exciting discussion at the

Army Research Office (ARO) workshop in early 2006 triggered the need for a new word to capture the idea of mechanochemical change in a rationally designed molecular unit. Credit for inventing the word "mechanophore" goes to Dr. Ken Caster, then at the ARO. The first recorded use of the term "mechanophore" appeared in a broad agency announcement (published July 2006) calling for proposals to the Department of Defense's Multidisciplinary University Research Initiative (MURI). Subsequently, we reported the mechanochemical ring-opening reaction of benzocyclobutane mechanophore to produce *ortho*-quinodimethide as the reactive intermediate.[24] Isotopic labeling experiments using a maleimide trap revealed that the mechanical force selectively promoted an orbital-symmetry-disallowed electrocyclic ring opening.[24] This work demonstrated the potential of polymer mechanochemistry to bias reaction pathways to favor outcomes that are not typically accessible via thermal or photochemical means. In addition, this work also answered, to a large extent, the question of how to align the directionality of mechanical force along the reaction coordinate of the molecular potential energy surface.[45]

The light-induced ring opening of spiropyrans had been demonstrated by the Bercovici group in the late 1960s.[46] The mechanochromism of small molecular spiropyran (e.g., upon grinding),[47] as well as spirobenzopyran-cross-linked polymer network,[48] were also reported. Inspired by these explorations, our team consisting of White, Sottos, Martínez, and Braun with funding from ARO advanced the idea of a spiropyran-based mechanophore, in which the spiro C−O bond is cleaved selectively upon mechanical activation and is accompanied by a change from colorless to purple (Figure 2).[22] At this time, we modified our synthetic strategies from coupling mechanophores to polymer chain ends to directly using mechanophores as bifunctional initiators for controlled radical polymerization.[49] We also greatly benefited from Percec's development of the single electron transfer-living radical polymerization (SET-LRP) that enabled high MW control in the 100 kDa range.[50]

The direct visualization of mechanochemical reactions under tensile stress in a "dog bone" specimen was indeed the starting point for the development of damage-sensing materials. Complementing our studies, the work led by Prof. Stephen Craig at Duke University benchmarked the use of single-molecule-force spectroscopy to characterize the molecular level changes in synthetic polymers under stress.[51]

Alongside our initial demonstrations, we have elucidated several factors that influence mechanical activation to provide insights into the nature of polymer mechanochemistry. These factors include structure−activity relationships,[52] environmental effects such as temperature,[53] polymer chain alignment and relaxation,[54] mechanophore orientation,[55] solvent swelling,[56] activation time dependence,[57] and loading conditions.[58] The reader interested in these topics is directed to a review previously published by our group.[31]

Our exploration of productive mechanochemistry continued with the development of a gem-dichlorocyclopropanated indene mechanoacid generator, which undergoes a force-induced rearrangement and subsequent elimination driven by aromatization to produce acid (Figure 2).[27] The mechanoacid design was conceived based on a report by Craig et al. that describes the mechanically activated rearrangement of *gem*-dihalocyclopropane to 2,3-dihaloalkenes.[59] This example is the only known mechanoacid reported to date. Because acid-catalyzed polymerization and cross-linking reactions such as polysiloxane formation,[60] epoxy resin curing,[61] novolac resin cross-linking,[62]

etc. are well-known, mechanoacids offer potential for designing mechanically triggered, autonomous self-healing materials when coupled with acid amplifier molecules.

We recently reported the mechanochemical production of phenyl cation[63] and depolymerization of end-capped poly(o-phthalaldehyde),[64] both of which experience heterolytic, rather than the usual homolytic, mechanically induced bond scission. Furthermore, in the latter example, we demonstrated that the depolymerization of cyclic poly(o-phthalaldehyde) produces monomer that repolymerizes, a true mechanochemical depolymerization rather than mechanical degradation of a polymer.

Our latest research illustrates a progression from solution-based and solid polymer blends to heterogeneous interfaces.[30] The demonstration of a mechanochemical [4 + 2] retro-cycloaddition of anthracene−maleimide cycloadduct at the interface of silica nanoparticle and polymer broadened the horizon of polymer mechanochemistry beyond chain-centered mechanophores and fostered the potential of self-healing composite materials.

## 3. THE MECHANOPHORE CONCEPT

Mechanophores are force-sensitive molecular units that respond to external mechanical fields by undergoing predictable chemical transformations. Successful design of mechanophores requires identification of key structural elements that enable mechanically induced reactions. Most of the mechanophores reported so far (Figure 3) contain a weak bond, a strained ring, or an isomerizable bond that selectively undergoes scission or changes conformation when stressed. Molecules that possess one of these structural features fall under the umbrella of suitable candidates for mechanophore design. It should be noted that molecules that decompose under mechanical stress into undesirable or unidentifiable compounds are not suitable to develop mechanophores.

The experimentally validated mechanophores reported to date are listed in Figure 3. The peroxide linkage reported by Encina and co-workers in 1980,[65] albeit not recognized as a mechanophore at that time, is included in the list since it indeed exhibits selective scission under mechanochemical activation. The types of mechanochemical reactions are generally categorized into three classes, that is, bond scission (cleavage of homolytic, heterolytic, or coordinate bond), pericyclic reactions, and isomerizations.

A common feature of mechanochemical reactions is the force-induced cleavage of one or more "weak bonds" (marked red in Figure 3) followed by other chemical transformations. What lowers the bond strength in each mechanophore class, however, differs case-by-case. When molecular strain builds up along the direction of the weak bond, intrinsically weak linkages such as the peroxide O−O bond (bond dissociation energy (BDE) ca. 35 kcal mol$^{-1}$),[65,23] diazo group (BDE ca. 24−30 kcal mol$^{-1}$),[21] disulfide bonds (BDE ca. 60 kcal mol$^{-1}$),[66] C−S bond of arylsulfonium salt (BDE ca. 65 kcal mol$^{-1}$),[63] and dative bonds (BDE ca. 36 kcal mol$^{-1}$ for palladium−phosphorus coordinative bond, BDE ca. 66 kcal mol$^{-1}$ for ruthenium−carbene coordinative bond, and BDE ca. 61 kcal mol$^{-1}$ for silver−carbene coordinative bond)[67,28,68,69] readily cleave and exhibit mechanochemical activity. For strong bonds with BDEs exceeding 72 kcal mol$^{-1}$ (e.g., C−O, C−C, and C−N bonds), a bond weakening strategy is generally employed to achieve mechanochemical selectivity. When strong bonds are incorporated into cyclic moieties, such as three[58,70] and four[24,71,72] membered rings and fused,[73,27] bridged,[74,75] and spiro[22,23]
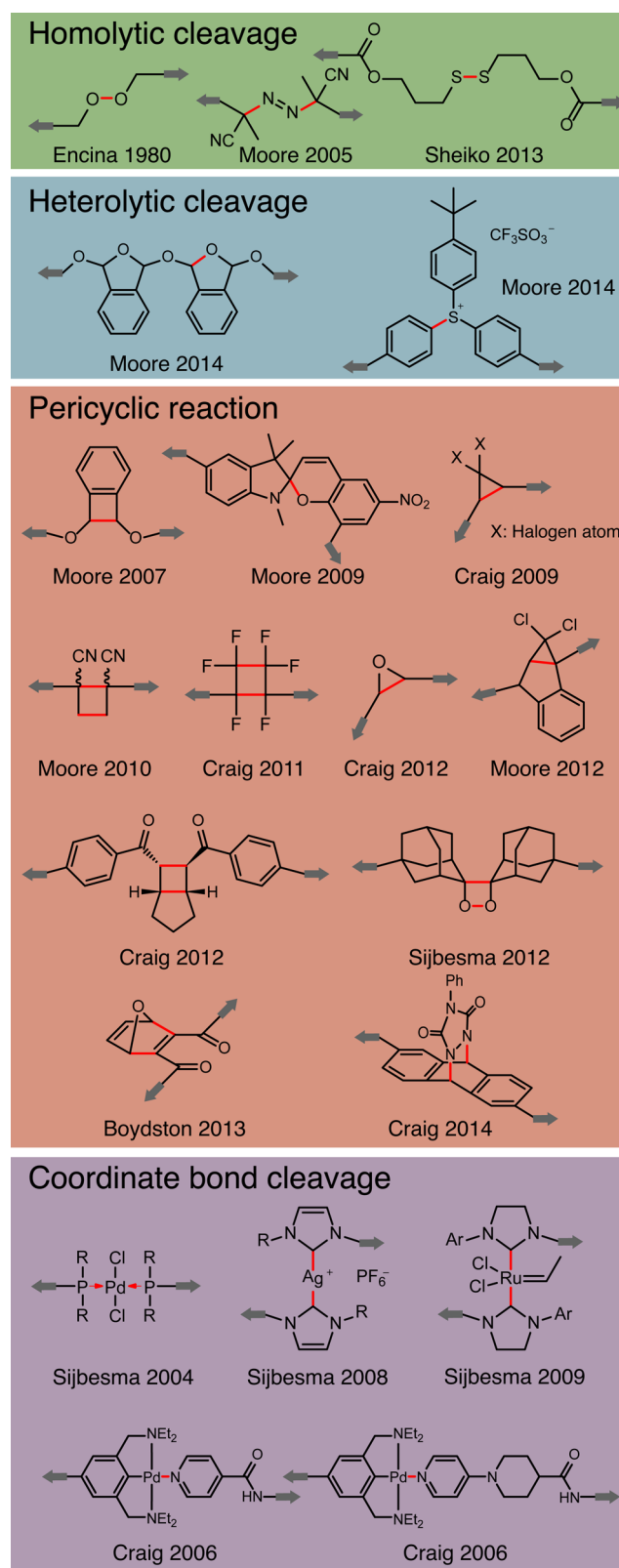


**Figure 3.** Mechanophore structures reported to date. The mechanochemically active bond is marked with red in each structure. Note: Mechanophores developed by the Bielawski group are not included pending resolution of ongoing disputes.

bicyclic rings, ring strain (and in some cases electronic factors as in spiropyran) significantly reduces otherwise high BDEs and differentiates the bond from the rest of chemical connections
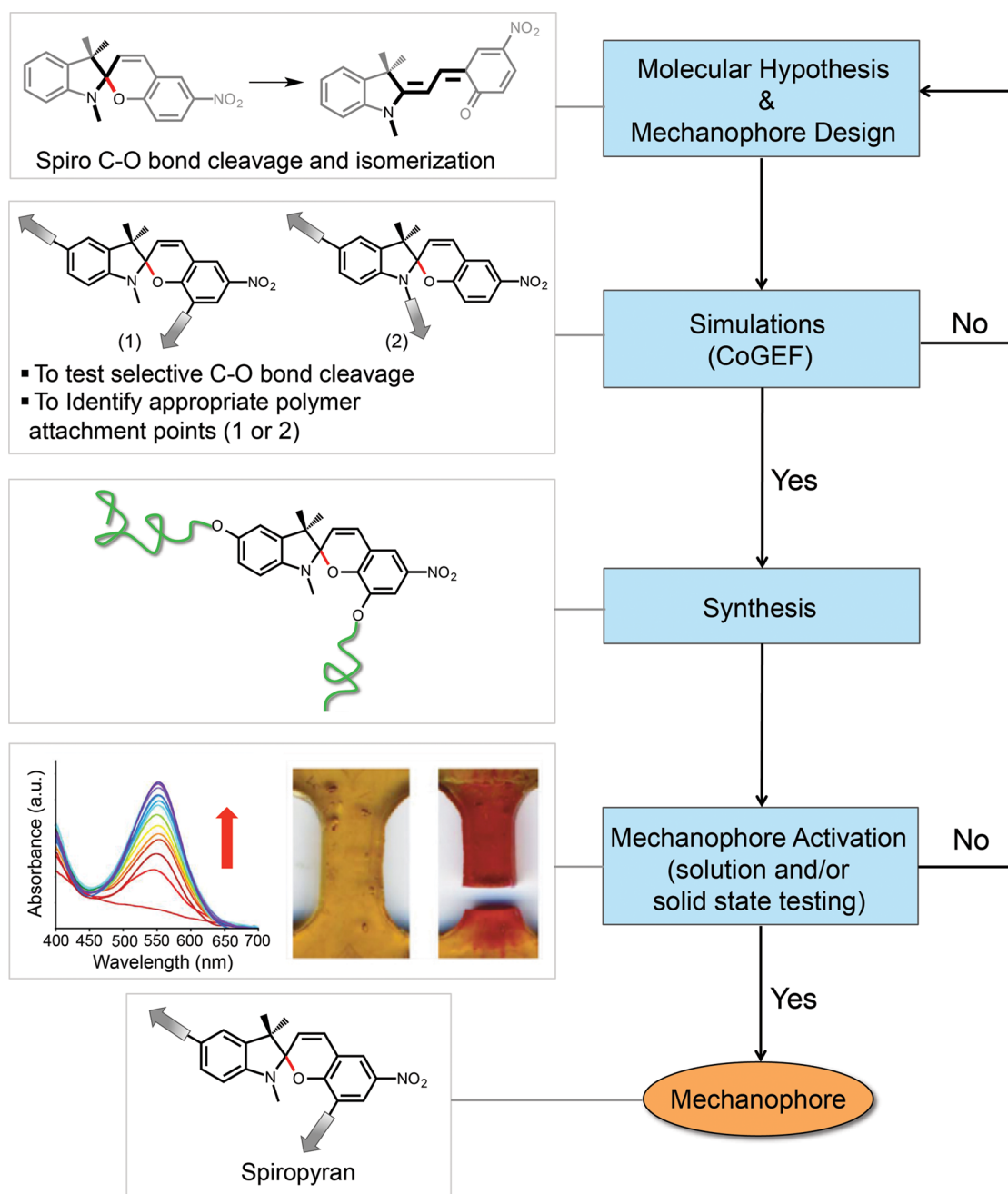
**Figure 4.** Workflow for the design, development, and evaluation of polymer-centered mechanophores. Section 4 discusses the design and development; an evaluation of mechanophore activation in both solution and solid state is discussed in Section 5.

within the molecule. Direct incorporation of a weak bond and strategic weakening of a strong bond form the molecular-level prerequisite of mechanochemical selectivity, and these approaches have been proven successful in the development of effective mechanophores. We emphasize that design strategy is not solely based on bond strength; the relationship of the target bond to the rest of the molecule, and the connectivity of the polymer chain to the mechanophore play important roles in selectively activating the target bond from all others (vide infra).

## 4. THE DESIGN AND DEVELOPMENT OF PUTATIVE MECHANOPHORES

The general workflow for the design and evaluation of polymer-centered mechanophores is presented in Figure 4, using the

spiropyran as a case study. The first step involves identifying a suitable mechanophore candidate based on a specific transformation and a specific bond whose scission is required to initiate the desired chemical change that results in color or fluorescence generation, pH change, free-radical formation, etc. Early in the design phase, we run CoGEF simulations[39] by systematically applying an elongational force and examining various pairs of polymer attachment points on the mechanophore. Exploration of points of attachment to the mechanophore as well as the positioning of mechanophores near the center of the polymer for efficient mechanochemical transduction is very important. For example, a spiropyran placed near the middle of two polymer chains is activated successfully upon being subjected to ultrasonication, whereas the spiropyran placed at the polymer chain end does not.[22] Moreover, if the connectivity

along the polymer backbone passes through the spiro-junction (structure 1 in Figure 4), the mechanophore is force-activated. In contrast, if the polymer connectivity does not include the spiro-junction (structure 2 in Figure 4), there is no force-activation.[22]

Given that the synthesis of mechanophores and their incorporation into polymers is tedious, we and others have come to use computer simulations to model the effect of external force on the mechanophore, which helps to rapidly screen mechanophores, as well as to identify the appropriate locations on the mechanophore to attach polymer chains. In CoGEF simulations, a small molecule mechanophore is first energy minimized and then a simulated force is applied to a pair of atoms on the mechanophore intended to become the points of attachments. Step-wise elongation of the distance between the two atoms followed by energy reminimization predicts which bonds are most likely cleaved as well as the energy required to break the bonds. If CoGEF calculations indicate that the desired bond is selectively cleaved under tensile force, then we proceed to synthesize the mechanophore and incorporate it into polymeric systems. Otherwise, the molecular hypothesis and mechanophore design are revised until a suitable candidate is identified. It is not uncommon for CoGEF calculations to reveal subtle and not so obvious distinctions in mechanochemical activation of mechanophores with different pairs of polymer attachment points. Presumably, the most sensitive pair of attachment points gives the best projection of the applied force vector onto the molecule's potential energy surface, coincident with the reaction coordinate.

## 5. EXPERIMENTAL VALIDATION OF PUTATIVE MECHANOPHORES

The mechanophore activation under mechanical force fields is tested in solution, in the solid state, or both. For a detailed summary of methods and techniques to test force-induced activation, the interested reader is directed to detailed summary in a recent review from our group.[32] Typical solution-phase experiments involve subjecting a dilute solution of mechanophore-centered polymers to ultrasonication. Dilute polymer solutions are used to avoid chain−chain interactions. Although ultrasonication was initially developed to serve as just a screening technique, it has become the most widely adopted method for testing mechanophore activation in solution because the ultrasonication experiments require only small quantities (milligrams) of material and mechanophore activation is conveniently monitored with readily available spectroscopic and analytical instrumentation (NMR, UV−vis, fluorescence, gel permeation chromatography (GPC), etc.). Given that there is only a single mechanophore per polymer molecule, the analytical quantification of mechanochemical changes is challenging, especially when high MW polymers are used. To tackle this issue, our group has effectively employed *in situ* trapping and isotopic labeling techniques to identify sonication products.[21,24] For solid-state testing, linear polymers or cross-linked polymer networks are molded into a "dog bone" shape and subjected to tensile loading, or compressed under pressure. Mechanophore activation is evaluated by monitoring the desired output response such as change in color (UV−vis absorbance) or fluorescence (fluorescence emission), acid release (pH), and free-radical generation (ESR spectroscopy).

A meticulous set of control experiments is crucial to validate the mechanochemical hypothesis and "mechanical" origin of mechanophore activation (Figure 5). A typical experimental setup consists of a mechanophore-centered macromolecule
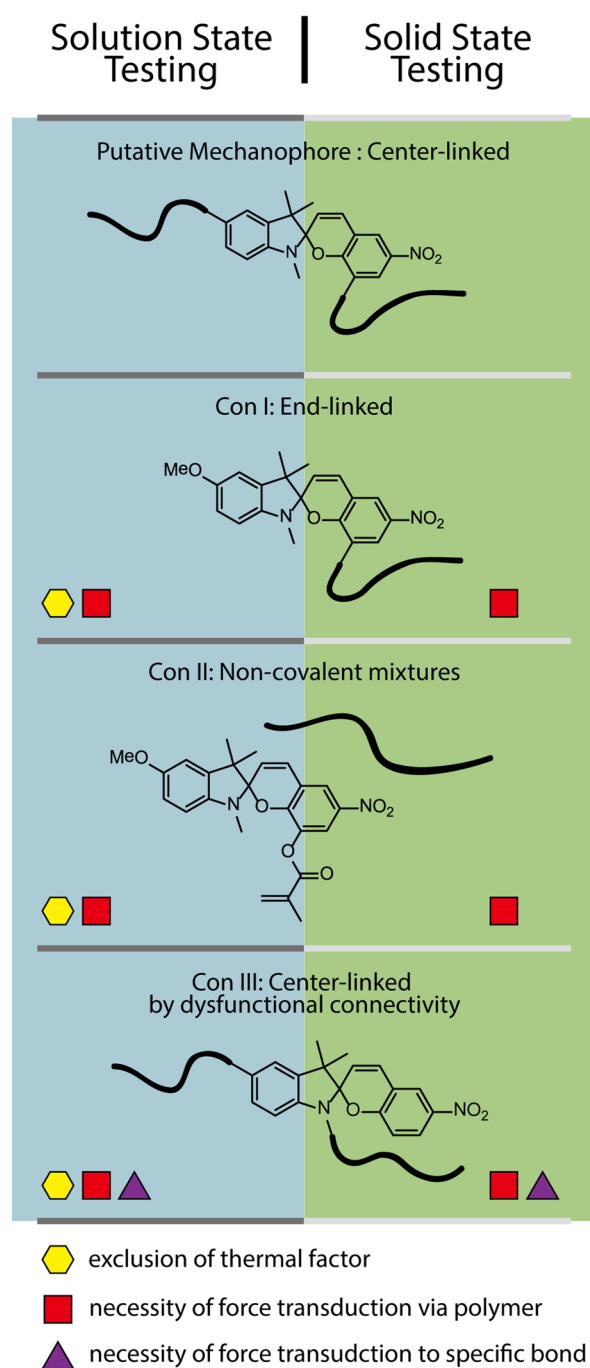


**Figure 5.** Common controls used in polymer mechanochemistry.

where two polymers are attached to specific atoms in the mechanophore. In spiropyran-linked polymer, poly(methyl acrylate) chains were connected to C5′ position of the indole and C8′ position of the benzopyran.[22] Three common controls used in polymer mechanochemistry research are a mechanophore-end-capped polymer (Con-I), a mixture of small molecular mechanophore and the polymer (Con-II), and a mechanophore-centered polymer with a dysfunctional connectivity (Con-III). An example of Con-III is a spiropyran-linked polymer with the polymer chains attached to the indole moiety at the C5′ and the N-position. While the target molecule exhibits the expected mechanochemical change (color change in case of spiropyran), failure to observe the change in case of Con-I, Con-II, and Con-III confirms the mechanochemical nature of the

reactions that the force transduction is inefficient if polymers are not attached at both ends of the mechanophore. Additionally, Con-II and Con-III capitulate that the efficient focus of mechanical force at the "weak bond" is a prerequisite for activation. For instance, the dysfunctional connection in spiropyran-centered polymers (Con-III) hinders transduction of the mechanical force to the weak spiro C−O bond, thereby retaining the spiro bicyclic structure upon activation. Under ultrasonication conditions, results from Con-I, Con-II, and Con-III definitively and collectively preclude localized heat as the cause of mechanochemical reaction. The strong correlation between solution and solid-state mechanophore activation results shows that ultrasonication of macromolecule solutions provides a valid way to screen mechanophores for mechanoresponsive materials. The design and usage of appropriate controls are equally important to unequivocally evaluate mechanochemical transformations in polymer mechanochemistry.

## 6. CONCLUSION AND FUTURE DIRECTIONS

This Account has highlighted historical events in the field of polymer chemistry and important achievements in our group for the topic of polymer mechanochemistry. The take-home message is that mechanical force, if properly used, is not necessarily destructive, but instead, has potential for productive use. More than a decade's research effort by our group and others has set the stage for the development of damage responsive, self-repairing materials using mechanosensitive polymers. This Account provides practically useful perspectives from our group on the development of polymer mechanochemistry, which we hope will help stimulate further interest and effort from a wider range of scientific researchers in related fields. We also want to thank all the help and inspiration along the way that fostered our understanding of how important communication, teaching, and research can influence one another.[76]

## ■ AUTHOR INFORMATION

**Corresponding Author**

*E-mail: jsmoore@uiuc.edu.

**Notes**

The authors declare no competing financial interest.

**Biographies**

**Jun Li** received his B.S. from Fudan University (Shanghai, China) in Department of Macromolecular Science (2012). He is now a Ph.D. candidate in Department of Chemistry in University of Illinois at Urbana−Champaign. He joined Professor Moore's group in 2012 and his research focuses on mechanochemistry at heterointerfaces and encapsulation of active organic molecules.

**Nagamani Chikkannagari** received a M.Sc. in Chemistry in 2006 from the University of Hyderabad, India, and a Ph.D. in Chemistry in 2011 from the University of Massachusetts—Amherst under the supervision of Prof. S. Thayumanavan. She worked as a process technology development engineer at Intel Corporation from 2011 to 2013 and later joined Professor Moore's group as a postdoctoral research associate. Her research focuses on developing new mechanoacids for self-healing applications.

**Jeffrey Moore** received his B.S. in Chemistry (1984) and Ph.D. in Materials Science and Engineering with Prof. Samuel Stupp (1989), both from the University of Illinois. He then went to Caltech as an NSF postdoctoral fellow working with Prof. Robert Grubbs. In 1990, he

joined the faculty at the University of Michigan in Ann Arbor and then in 1993 returned to UIUC where he is currently the Murchison-Mallory Chair in the Department of Chemistry. Jeff is a Fellow of the American Academy of Arts & Sciences and the American Chemical Society; he received the Campus Award for Excellence in Undergraduate Teaching and has been recognized as a "Faculty Ranked Excellent by their Students". For 14 years, he served as an Associate Editor for the *Journal of the American Chemical Society*. In 2014, he was selected as an HHMI Professor. He has published on topics from technology in the classroom to self-healing polymers, mechanoresponsive materials, and shape-persistent macrocycles.

## ■ REFERENCES

(1) Gil, E. S.; Hudson, S. M. Stimuli-Reponsive Polymers and Their Bioconjugates. *Prog. Polym. Sci.* **2004**, *29*, 1173−1222.

(2) Mano, J. F. Stimuli-Responsive Polymeric Systems for Biomedical Applications. *Adv. Eng. Mater.* **2008**, *10*, 515−527.

(3) Ganta, S.; Devalapally, H.; Shahiwala, A.; Amiji, M. A Review of Stimuli-Responsive Nanocarriers for Drug and Gene Delivery. *J. Controlled Release* **2008**, *126*, 187−204.

(4) Klaikherd, A.; Nagamani, C.; Thayumanavan, S. Multi-Stimuli Sensitive Amphiphilic Block Copolymer Assemblies. *J. Am. Chem. Soc.* **2009**, *131*, 4830−4838.

(5) Jochum, F. D.; Theato, P. Temperature- and Light-Responsive Smart Polymer Materials. *Chem. Soc. Rev.* **2013**, *42*, 7468−7483.

(6) Zhao, Y. Light-Responsive Block Copolymer Micelles. *Macromolecules* **2012**, *45*, 3647−3657.

(7) Katz, J. S.; Burdick, J. A. Light-Responsive Biomaterials: Development and Applications. *Macromol. Biosci.* **2010**, *10*, 339−348.

(8) Schmaljohann, D. Thermo- and pH-Responsive Polymers in Drug Delivery. *Adv. Drug Delivery Rev.* **2006**, *58*, 1655−1670.

(9) Du, J. Z.; Du, X. J.; Mao, C. Q.; Wang, J. Tailor-Made Dual pH-Sensitive Polymer-Doxorubicin Nanoparticles for Efficient Anticancer Drug Delivery. *J. Am. Chem. Soc.* **2011**, *133*, 17560−17563.

(10) Huh, K. M.; Kang, H. C.; Lee, Y. J.; Bae, Y. H. pH-Sensitive Polymers for Drug Delivery. *Macromol. Res.* **2012**, *20*, 224−233.

(11) Wen, Y. T.; Zhang, Z. X.; Li, J. Highly Efficient Multifunctional Supramolecular Gene Carrier System Self-Assembled from Redox-Sensitive and Zwitterionic Polymer Blocks. *Adv. Funct. Mater.* **2014**, *24*, 3874−3884.

(12) Cho, H.; Bae, J.; Garripelli, V. K.; Anderson, J. M.; Jun, H. W.; Jo, S. Redox-Sensitive Polymeric Nanoparticles for Drug Delivery. *Chem. Commun.* **2012**, *48*, 6043−6045.

(13) Huang, H.; Kamm, R. D.; Lee, R. T. Cell Mechanics and Mechanotransduction: Pathways, Probes, and Physiology. *Am. J. Physiol. Cell Physiol.* **2004**, *287*, C1−C11.

(14) Comrie, J. E.; Huck, W. T. S. Exploring Actuation and Mechanotransduction Properties of Polymer Brushes. *Macromol. Rapid Commun.* **2008**, *29*, 539−546.

(15) Goodman, M. B.; Lumpkin, E. A.; Ricci, A.; Tracey, W. D.; Kernan, M.; Nicolson, T. Molecules and Mechanisms of Mechanotransduction. *J. Neurosci.* **2004**, *24*, 9220−9222.

(16) Gillespie, P. G.; Walker, R. G. Molecular Basis of Mechanosensory Transduction. *Nature* **2001**, *413*, 194−202.

(17) Staudinger, H.; Bondy, H. F. Isoprene and Rubber. XIX. The Molecular Size of Rubber and Balata. *Ber. Dtsch. Chem. Ges. B* **1930**, *63*, 734−736.

(18) Staudinger, H.; Leupold, E. O. Isoprene and Rubber. XVIII. Studies of the Viscosity of Balata. *Ber. Dtsch. Chem. Ges. B* **1930**, *63*, 730−733.

(19) Staudinger, H.; Hener, W. Highly Polymerized Compounds. XCIII. The Breaking Up of the Molecular Fibers of the Polystyrenes. *Ber. Dtsch. Chem. Ges. B* **1934**, *67*, 1159−1164.

(20) Sohma, J. Mechanochemistry of Polymers. *Prog. Polym. Sci.* **1989**, *14*, 451−596.

(21) Berkowski, K. L.; Potisek, S. L.; Hickenboth, C. R.; Moore, J. S. Ultrasound-Induced Site-Specific Cleavage of Azo-Functionalized Poly(ethylene glycol). *Macromolecules* **2005**, *38*, 8975−8978.

(22) Davis, D. A.; Hamilton, A.; Yang, J.; Cremar, L. D.; Gough, D. V.; Potisek, S. L.; Ong, M. T.; Braun, P. V.; Martínez, T. J.; White, S. R.; Moore, J. S.; Sottos, N. R. Force-Induced Activation of Covalent Bonds in Mechanoresponsive Polymeric Materials. *Nature* **2009**, *459*, 68−72.

(23) Chen, Y. L.; 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*, 559−562.

(24) 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*, 423−427.

(25) Lenhardt, J. M.; Ong, M. T.; Choe, R.; Evenhuis, C. R.; Martínez, T. J.; Craig, S. L. Trapping a Diradical Transition State by Mechanochemical Polymer Extension. *Science* **2010**, *329*, 1057−1060.

(26) Larsen, M. B.; Boydston, A. "Flex-Activated" Mechanophores: Using Polymer Mechanochemistry To Direct Bond Bending Activation. *J. Am. Chem. Soc.* **2013**, *135*, 8189−8192.

(27) Diesendruck, C.; Steinberg, B. D.; Sugai, N.; Silberstein, M. N.; Sottos, N. R.; White, S. R.; Braun, P. V.; Moore, J. S. Proton-Coupled Mechanochemical Transduction: A Mechanogenerated Acid. *J. Am. Chem. Soc.* **2012**, *134*, 12446−12449.

(28) Piermattei, A.; Karthikeyan, S.; Sijbesma, R. P. Activating Catalysts with Mechanical Force. *Nat. Chem.* **2009**, *1*, 133−137.

(29) Tennyson, A. G.; Wiggins, K. M.; Bielawski, C. W. Mechanical Activation of Catalysts for C-C bond Forming and Anionic Polymerization Reactions from a Single Macromolecular Reagent. *J. Am. Chem. Soc.* **2010**, *132*, 16631−16636.

(30) Li, J.; Shiraki, T.; Hu, B.; Wright, R. A. E.; Zhao, B.; Moore, J. S. Mechanophore Activation at Heterointerfaces. *J. Am. Chem. Soc.* **2014**, *136*, 15925−15928.

(31) Caruso, M. M.; Davis, D. A.; Shen, Q.; Odom, S. A.; Sottos, N. R.; White, S. R.; Moore, J. S. Mechanically-induced Chemical Changes in Polymeric Materials. *Chem. Rev.* **2009**, *109*, 5755−5798.

(32) May, P. A.; Moore, J. S. Polymer Mechanochemistry: Techniques to Generate Molecular Force via Elongational Flows. *Chem. Soc. Rev.* **2013**, *42*, 7497−7506.

(33) Beyer, M. K.; Clausen-Schaumann, H. Mechanochemistry: The Mechanical Activation of Covalent Bonds. *Chem. Rev.* **2005**, *105*, 2921−2948.

(34) Black, A. L.; Lenhardt, J. M.; Craig, S. L. From Molecular Mechanochemistry to Stress-Responsive Materials. *J. Mater. Chem.* **2011**, *21*, 1655−1663.

(35) Kauzmann, W.; Eyring, H. The Viscous Flow of Large Molecules. *J. Am. Chem. Soc.* **1940**, *62*, 3113−3125.

(36) Melville, H. W.; Murray, A. J. R. The Ultrasonic Degradation of Polymers. *Trans. Faraday Soc.* **1950**, *46*, 996−1009.

(37) Culter, J. D.; Zakin, J. L.; Patterson, G. K. Mechanical Degradation of Dilute Solutions of High Polymers in Capillary Tube Flow. *J. Appl. Polym. Sci.* **1975**, *19*, 3235−3240.

(38) Horn, A. F.; Merrill, E. W. Midpoint Scission of Macromolecules in Dilute Solution in Turbulent Flow. *Nature* **1984**, *312*, 140−141.

(39) Bretzlaff, R. S.; Wool, R. P. Frequency Shifting and Asymmetry in Infrared Bands of Stressed Polymers. *Macromolecules* **1983**, *16*, 1907−1917.

(40) Rule, J. D.; Wilson, S. R.; Moore, J. S. Radical Polymerization Initiated by Bergman Cyclization. *J. Am. Chem. Soc.* **2003**, *125* (43), 12992−12993.

(41) Beyer, M. K. The Mechanical Strength of a Covalent Bond Calculated by Density Functional Theory. *J. Chem. Phys.* **2000**, *112*, 7307−7312.

(42) Beyer, M. K.; Clausen-Schaumann, H. S. Mechanochemistry: The Mechanical Activation of Covalent Bonds. *Chem. Rev.* **2005**, *105*, 2921−2948.

(43) Yount, W. C.; Loveless, D. M.; Craig, S. L. Small-molecule Dynamics and Mechanisms Underlying the Macroscopic Mechanical Properties of Coordinatively Cross-linked Polymer Networks. *J. Am. Chem. Soc.* **2005**, *127*, 14488−14496.

(44) Ong, M. T.; Leiding, J.; Tao, H. L.; Virshup, A. M.; Martínez, T. J. First Principles Dynamics and Minimum Energy Pathways for Mechanochemical Ring Opening of Cyclobutene. *J. Am. Chem. Soc.* **2009**, *131*, 6377−6379.

(45) Evans, E. Probing the Relation between Force-lifetime and Chemistry in Single Molecular Bonds. *Annu. Rev. Biophys. Biomol. Struct.* **2001**, *30*, 105−128.

(46) Bercovici, T.; Fischer, E. Photosensitized Coloration of Photochromic Spiropyrans. *J. Am. Chem. Soc.* **1964**, *86*, 5687−5688.

(47) Tipikin, D. S. Mechanochromism of Organic Compounds by the Example of Spiropyran. *Russ. J. Phys. Chem.* **2001**, *75*, 1720−1722.

(48) Smets, G.; Blauwe, F. D. Chemical Reactions in Solid Polymeric Systems. Photomechanical Phenomena. *Pure Appl. Chem.* **1974**, *39*, 1−2.

(49) 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*, 13808−13809.

(50) Rosen, B. M.; Percec, V. Single-Electron Transfer and Single-Electron Transfer Degenerative Chain Transfer Living Radical Polymerization. *Chem. Rev.* **2009**, *109*, 5069−5199.

(51) Wu, D.; Lenhardt, J. M.; Black, A. L.; Akhremitchev, B. B.; Craig, S. L. Molecular Stress Relief through a Force-Induced Irreversible Extension in Polymer Contour Length. *J. Am. Chem. Soc.* **2010**, *132*, 15936−15938.

(52) Kryger, M. J.; Munaretto, A. M.; Moore, J. S. Structure−Mechanochemical Activity Relationships for Cyclobutane Mechanophores. *J. Am. Chem. Soc.* **2011**, *133*, 18992−18998.

(53) Beiermann, B. A.; Davis, D. A.; Kramer, S. L.; Moore, J. S.; Sottos, N. R.; White, S. R. Environmental Effects on Mechanochemical Activation of Spiropyran in Linear PMMA. *J. Mater. Chem.* **2011**, *21*, 8443−8447.

(54) Beiermann, B. A.; Kramer, S. L.; May, P. A.; Moore, J. S.; White, S. R.; Sottos, N. R. The Effect of Polymer Chain Alignment and Relaxation on Force-Induced Chemical Reactions in an Elastomer. *Adv. Funct. Mater.* **2014**, *24*, 1529−1537.

(55) Beiermann, B. A.; Kramer, S. L.; Moore, J. S.; White, S. R.; Sottos, N. R. Role of Mechanophore Orientation in Mechanochemical Reactions. *ACS Macro Lett.* **2012**, *1*, 163−166.

(56) Lee, C. K.; Diesendruck, C. E.; Lu, E.; Pickett, A. N.; May, P. A.; Moore, J. S.; Braun, P. V. Solvent Swelling Activation of a Mechanophore in a Polymer Network. *Macromolecules* **2014**, *47*, 2690−2694.

(57) Lee, C. K.; Davis, D. A.; White, S. R.; Moore, J. S.; Sottos, N. R.; Braun, P. V. Force-Induced Redistribution of a Chemical Equilibrium. *J. Am. Chem. Soc.* **2010**, *132*, 16107−16111.

(58) Grady, M. E.; Beiermann, B. A.; Moore, J. S.; Sottos, N. R. Shockwave loading of Mechanochemically Active Polymer Coatings. *ACS Appl. Mater. Interfaces* **2014**, *6*, 5350−5355.

(59) Lenhardt, J. M.; Black, A. L.; Craig, S. L. gem-Dichlorocyclopropanes as Abundant and Efficient Mechanophores in Polybutadiene Copolymers under Mechanical Stress. *J. Am. Chem. Soc.* **2009**, *131*, 10818−10819.

(60) Shinozuka, T.; Shirai, M.; Tsunooka, M. Polymers as Sulfonic Acid Generator on Irradiation at 146 nm. *Eur. Polym. J.* **2001**, *37*, 1625−1634.

(61) Dearborn, E. C.; Fuoss, R. M.; White, A. F. Acid Acceleration of Epoxide Condensations. *J. Polym. Sci.* **1955**, *16*, 201−208.

(62) Liu, H.; Chen, W.; Wu, F. Characterization of Negative Tone Photoresist Based on Acid Catalyzed Dehydration Crosslinking of Novolac Resins Having Pendant Carboxyl Groups. *J. Polym. Res.* **2002**, *9*, 251−256.

(63) Shiraki, T.; Diesendruck, C. E.; Moore, J. S. The Mechanochemical Production of Phenyl Cations through Heterolytic Bond Scission. *Faraday Discuss.* **2014**, *170*, 385−394.

(64) 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*, 623−628.

(65) Encina, M. V.; Sarasúa, M.; Gargallo, L.; Radic, D. Ultrasonic Degradation of Polyvinylpyrrolidone: Effect of Peroxide Linkages. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 757−760.

(66) Li, Y. C.; Nese, A.; Matyjaszewski, K.; Sheiko, S. S. Molecular Tensile Machines: Anti-Arrhenius Cleavage of Disulfide Bonds. *Macromolecules* **2013**, *46*, 7196−7201.

(67) Paulusse, J. M. J.; Sijbesma, R. P. Selectivity of Mechanochemical Chain Scission in Mixed Palladium (II) and Platinum (II) Coordination Polymers. *Chem. Commun.* **2008**, 4416−4418.

(68) Karthikeyan, S.; Potisek, S. L.; Piermattei, P. A.; Sijbesma, R. P. Highly Efficient Mechanochemical Scission of Silver-Carbene Coordination Polymers. *J. Am. Chem. Soc.* **2008**, *130*, 14968−14969.

(69) Kersey, F. R.; Yount, W. C.; Craig, S. L. Single-Molecule Force Spectroscopy of Biomolecular Reactions: System Homology in the Mechanical Activation of Ligand Substituteion Reactions. *J. Am. Chem. Soc.* **2006**, *128*, 3886−3887.

(70) Klukovich, H. M.; Kean, Z. S.; Ramirez, A. L. B.; Lenhardt, J. M.; Lin, J. X.; Hu, X. Q.; Craig, S. L. Tension Trapping of Carbonyl Ylides Facilitated by a Change in Polymer Backbone. *J. Am. Chem. Soc.* **2012**, *134*, 9577−9580.

(71) Kryger, M. J.; Ong, M. T.; Odom, S. A.; Sottos, N. R.; White, S. R.; Martinez, T. J.; Moore, J. S. Masked Cyanoacrylates Unveiled by Mechanical Force. *J. Am. Chem. Soc.* **2010**, *132*, 4558−4559.

(72) Klukovich, H. M.; Kean, Z. S.; Lacono, S. T.; Craig, S. L. Mechanically Induced Scission and Subsequent Thermal Remending of Perfluorocyclobutane Polymers. *J. Am. Chem. Soc.* **2011**, *133*, 17882−17888.

(73) Kean, Z. S.; Ramirez, B.; Yan, Y. F.; Craig, S. L. Bicyclo[3.2.0]-heptane Mechanophores for the Non-scissile and Photochemically Reversible Generation of Reactive Bis-enones. *J. Am. Chem. Soc.* **2012**, *134*, 12939−12942.

(74) Larsen, M. B.; Boydston, A. J. Flex-Activated" Mechanophores: Using Polymer Mechanochemistry to Direct Bond Bending Activation. *J. Am. Chem. Soc.* **2013**, *135*, 8189−8192.

(75) Gossweiler, G. R.; Hewage, G. B.; Soriano, G.; Wang, Q. M.; Welshofer, G. W.; Zhao, X. H.; Graig, S. L. Mechanochemical Activation of Covalent Bonds in Polymers with Full and Repeatable Macroscopic Shape Recovery. *ACS Macro Lett.* **2014**, *3*, 216−219.

(76) YouTube video: Force-Activated Electrocyclic Rearrangements (8.8) https://www.youtube.com/watch?v=pXeFgumvpd8. Accessed May 12, 2015.