

HIGHLIGHT

Forcing Ladderenes into Plastic Semiconductors with Mechanochemistry

Samuel W. Thomas III^[a]

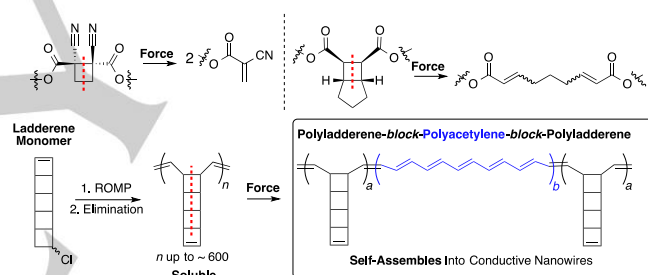
Stimuli responsive polymers convert environmental inputs into pre-programmed changes in properties of interest through stimulus-induced alterations in covalent bonding and non-covalent interactions. Examples of target applications of this broad class of materials include sensors, actuators, drug-delivery systems, and self-healing materials. Mechanical force has been known for many decades to break covalent bonds of polymers, causing their degradation. More recently, however, a number of research groups have harnessed the potential of mechanical force towards rationally designed "productive" mechanochemistry, in which chemical reactions of polymers, induced by mechanical force, yield desirable changes in properties or reactivity.^[1,2] In addition to fundamental insights in how force induces unusual chemical reactivity, mechanochemistry is of emerging importance in stimuli-responsive materials: there are reports of polymers that change color, release acid, show chemiluminescence, or catalyze olefin metathesis reactions due to mechanochemical cleavage of specific chemical bonds.^[1,2]

One of the key organizing principles in polymer mechanochemistry is the concept of a "mechanophore"—a structural moiety that responds predictably to mechanical force, much as a chromophore responds predictably to irradiation with light. Mechanophores usually include bonds that are either intrinsically weak such as disulfides or azo groups, or are weakened by inclusion in a strained ring that opens during the mechanochemical reaction. Four-member carbocycles undergoing formal cycloreversions or electrocyclic ring openings have emerged as a leading class of mechanophores.^[3-6]

Conjugated polymers, which contain continuously conjugated delocalized orbitals along their main chains, constitute a different class of functional polymeric materials. Polyacetylene is a prototypical conjugated polymer; its discovery and remarkable increase in conductivity upon doping^[7] initiated intense research in the area and resulted in awarding of the Nobel Prize in 2000. A wide variety of conjugated polymers now enjoy extensive utility in a variety of optoelectronic applications, including organic light emitting devices, transistors, and photovoltaics. Up until this point have been no examples of mechanically transforming insulating polymers to conjugated polymers, which would confer drastic changes in a range of properties upon exertion of force. A recent collaborative paper from the Xia, Burns and Martinez groups at Stanford, however, blazes a new trail connecting these heretofore distinct, but cutting edge classes of polymers.^[8]

The monomers used in this work comprise five fused cyclobutyl rings that adopt a staircase-like conformation, known

as a ladderene. The strain present in the ladderene monomer used in this example elegantly serves two purposes. First, it plays an active role in the successful preparation of the mechanically sensitive polymer. Relief of ring strain of the terminal cyclobutene ring of the [5]ladderene monomer **1** (see Scheme 1 provides driving force for ring opening metathesis polymerization (ROMP) initiated by the Grubbs Generation III ruthenium carbene metathesis catalyst. Post-polymerization dehydrohalogenation yielded hydrocarbon homopolymers with an extraordinarily high loading of mechanophores present along the polymer backbone—not only does every repeat unit have a mechanophore present, but each mechanophore can break up to four C-C bonds. In addition, the controlled nature of the ROMP polymerization enabled the preparation of three samples with different molecular weights, which were important for evidence of mechanochemistry (*vide infra*).



Scheme 1. Top: Two previous examples of mechanochemical cycloreversions of cyclobutanes within polymers.^[4,6] Bottom: Mechanochemistry of poly(ladderene) to yield polyacetylene discussed here.

The authors used ultrasonication to investigate polymer mechanochemistry, which is a common method for exposing polymer chains to mechanical forces necessary for promoting chemical reactions through acoustic cavitation.^[9] A picture of their striking results is shown in Figure 1; within seconds, polymer solutions turn blue, which becomes more intense over time. Evidence from electronic absorbance spectra, ¹³C NMR, and resonant Raman spectra confirm all-*trans* polyacetylenes as the mechanochemical product, with long conjugation lengths of greater than 100 conjugated alkene units. The authors support a mechanism of ladderene "unzipping" with theoretical calculations indicating that the four sigma bonds of the ladderene are broken in two steps, with each step constituting a formal [2+2] cycloreversion; the product of only one cycloreversion is a metastable intermediate. The result is an "all-or-nothing" reaction, with fully zipped (four fused cyclobutyl rings in the ladderene) or unzipped (no cyclobutyl rings) mechanophores as the only isolable states.

Claims of mechanochemical reactivity during sonication require ruling out thermal activation as a potential mechanism. Consistent with known structure-property relationships of analogous mechanochemically-sensitive polymers, the authors

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here observed a positive correlation between degree of polymerization and the observed rate of polyacetylene formation—longer polymer chains produced polyacetylene faster during sonication than shorter polymer chains. On the other hand, rates of unimolecular, thermally promoted reactions along polymer main chains do not depend on the degree of polymerization.

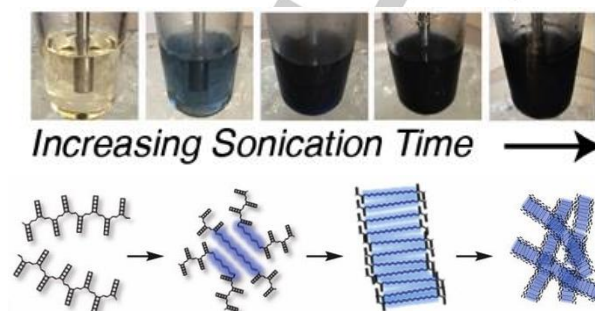
Another unique organizing principle of polymer mechanochemistry is the positional dependence of mechanophore sensitivity that results from uneven distribution of force along polymer chains. The result is that mechanophores in the middle portion of chains may react during sonication, while those at or near the chain ends do not. Combining the high loading of mechanophore along the polymer chain with this positional dependence leads to mechanically-induced formation of triblock copolymers, in which the central block is insoluble, semiconducting polyacetylene, while the outer blocks are soluble, electrically insulating poly ladderene units. The authors characterized this unique topology through observation of self assembled nanostructures—micelles that transform into interconnected nanowires with increased conversion—by dynamic light scattering and transmission electron microscopy.

This work presents numerous unique and impactful characteristics, including: i) The coupling of mechanical stimuli with an increase in conductivity and changes in optical properties brings to mind a number of potential applications in which force is transduced into electrical signal using organic polymer, including pressure sensing on small scales. ii) The successful integration of the captivating ladderene moiety as the key majority component of a functional polymeric material is unique and represents a beautiful merging of chemical form and function. iii) These materials are examples of only a small number of polymers in the literature that have high loadings of mechanophores, enabling future force-induced self assembly of functional polymers by taking advantage of the positional dependence of polymer mechanochemistry. iv) Unzipping of the ladderene moieties to polyacetylenes yields a large increases in chain length upon application of force, raising the potential for similar strategies to yield molecular “slack” for mitigation of polymer failure.^[10] v) It is important to distinguish this work, which demonstrates a novel polymer-to-polymer transition using pulling forces in solution, from several previous reports that describe ball milling as an approach for the synthesis of conjugated polymers from monomers.^[11,12]

A primary drawback of these unzipping poly ladderenes, however, is the quantity of materials produced, which is reported in the paper on the order of tens of milligrams. Polymers with similarly remarkable force-responsive optoelectronic properties but with syntheses that allowed significant scale-up would push the development of these materials toward real-world impact. In addition, although force-responsive conductivity of the block copolymer nanostructures was observed, the conductivity was rather low. Approaches towards increasing the contrast in electronic properties between unstressed and stressed, or designing a reversible optoelectronic mechanophore would increase the future potential of these materials. Alternative designs in mechanophore monomers would likely improve electronic properties and synthetic accessibility. These potential directions for future investigations aside, this highly innovative work combines previously distinct areas of physical organic chemistry—polymer mechanochemistry, conjugated polymers, S. W. Thomas, *Angew. Chem. Int. Ed.* **2017**, *56*, 15196.

and ladderenes—into a new class of stimuli-responsive functional materials that is certain to inspire chemists and material scientists.

Figure 1. Effects of mechanical force resulting from ultrasonication on a poly ladderene. *Top:* Photographs of blue color and polymer insolubility, characteristic of polyacetylene, developing during sonication. *Bottom:* Schematic of force-induced aggregation of insoluble polyacetylene blocks. Adapted from reference [8]. Reprinted with permission from AAAS.



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Keywords: polymer mechanochemistry • ladderene • polyacetylene • block copolymer • conducting polymers

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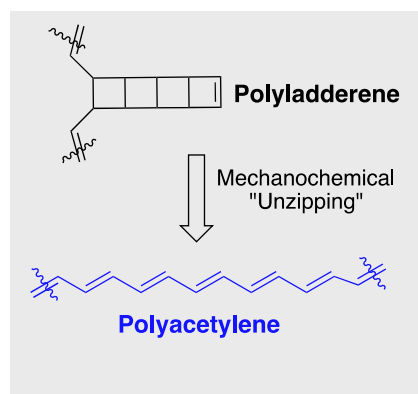
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Layout 1:

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Xia, Burns, Martinez, and coworkers harnessed the ring strain of ladderenes to enable both their polymerization and mechanochemical unzipping to yield semiconducting polyacetylene-based block copolymers. These materials have promise as functional polymers for applications such as detection of physical stress.



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