

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188		
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>					
1. REPORT DATE (DD-MM-YYYY)		2. REPORT TYPE New Reprint		3. DATES COVERED (From - To) -	
4. TITLE AND SUBTITLE Mechanochemical strengthening of a synthetic polymer in response to typically destructive shear forces			5a. CONTRACT NUMBER W911NF-07-1-0409		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER 611103		
6. AUTHORS Ashley L. Black Ramirez, Zachary S. Kean, Joshua A. Orlicki, Mangesh Champhekar, Sarah M. Elsagr, Wendy E. Krause, Stephen L. Craig			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES University of Illinois - Urbana c/o OSPRA 1901 S. First Street, Suite A Champaign, IL 61820 -7406			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSOR/MONITOR'S ACRONYM(S) ARO		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) 52530-CH-MUR.51		
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT High shear stresses are known to trigger destructive bond-scission reactions in polymers. Recent work has shown that the same shear forces can be used to accelerate non-destructive reactions in mechanophores along polymer backbones, and it is demonstrated here that such mechanochemical reactions can be used to strengthen a polymer subjected to otherwise destructive shear forces. Polybutadiene was functionalized with dibromocyclopropane mechanophores, whose mechanical activation generates allylic bromides that are crosslinked in situ by nucleophilic substitution reactions with carboxylates. The crosslinking is activated efficiently by shear forces both in solution					
15. SUBJECT TERMS synthetic polymers					
16. SECURITY CLASSIFICATION OF:		17. LIMITATION OF ABSTRACT		15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU	UU		Jeffrey Moore
				19b. TELEPHONE NUMBER 217-244-5289	

Report Title

Mechanochemical strengthening of a synthetic polymer in response to typically destructive shear forces

ABSTRACT

High shear stresses are known to trigger destructive bond-scission reactions in polymers. Recent work has shown that the same shear forces can be used to accelerate non-destructive reactions in mechanophores along polymer backbones, and it is demonstrated here that such mechanochemical reactions can be used to strengthen a polymer subjected to otherwise destructive shear forces. Polybutadiene was functionalized with dibromocyclopropane mechanophores, whose mechanical activation generates allylic bromides that are crosslinked in situ by nucleophilic substitution reactions with carboxylates. The crosslinking is activated efficiently by shear forces both in solvated systems and in bulk materials, and the resulting covalent polymer networks possess moduli that are orders-of-magnitude greater than those of the unactivated polymers.

These molecular-level responses and their impact on polymer properties have implications for the design of materials that, like biological materials, actively remodel locally as a function of their physical environment.

REPORT DOCUMENTATION PAGE (SF298)
(Continuation Sheet)

Continuation for Block 13

ARO Report Number 52530.51-CH-MUR
Mechanochemical strengthening of a synthetic p...

Block 13: Supplementary Note

© 2013 . Published in Nature Chemistry, Vol. Ed. 0 5, (9) (2013), (, (9). DoD Components reserve a royalty-free, nonexclusive and irrevocable right to reproduce, publish, or otherwise use the work for Federal purposes, and to authorize others to do so (DODGARS §32.36). The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

Approved for public release; distribution is unlimited.

Mechanochemical strengthening of a synthetic polymer in response to typically destructive shear forces

Ashley L. Black Ramirez¹, Zachary S. Kean¹, Joshua A. Orlicki², Mangesh Champhekar³, Sarah M. Elsagr¹, Wendy E. Krause³ and Stephen L. Craig^{1*}

High shear stresses are known to trigger destructive bond-scission reactions in polymers. Recent work has shown that the same shear forces can be used to accelerate non-destructive reactions in mechanophores along polymer backbones, and it is demonstrated here that such mechanochemical reactions can be used to strengthen a polymer subjected to otherwise destructive shear forces. Polybutadiene was functionalized with dibromocyclopropane mechanophores, whose mechanical activation generates allylic bromides that are crosslinked *in situ* by nucleophilic substitution reactions with carboxylates. The crosslinking is activated efficiently by shear forces both in solvated systems and in bulk materials, and the resulting covalent polymer networks possess moduli that are orders-of-magnitude greater than those of the unactivated polymers. These molecular-level responses and their impact on polymer properties have implications for the design of materials that, like biological materials, actively remodel locally as a function of their physical environment.

Materials typically break down in response to repeated cycles of mechanical load and stress that they experience during use. In polymer solutions, for example, shear-induced bond breaking reduces molecular weight and leads to a loss in viscosity¹, a problem that plagues oils and lubricants in high-performance engines². In solid-state applications, stress-induced bond scission or chain slippage triggers the formation of microcracks that propagate and eventually lead to material failure³. Many biological materials, however, remodel and become stronger in direct response to the mechanical forces that otherwise might cause them to fail. Bone and muscle, for example, build mass and strength when subjected to load, and wood⁴ and hair⁵ respond to force-induced bond breaking at the molecular level by forming new bonds in the strained conformation, which results in a net increase in strength. Here, we report a family of synthetic polymers in which the same forces responsible for the destructive processes of bond scission and chain disentanglement are channelled into constructive, bond-forming reactions. The response, to which we refer for convenience as activated remodelling via mechanochemistry (ARM), requires no additional external stimulus or energy input beyond the imposed shear, and functions in both solution and bulk, to form molecularly remodelled polymer gels and crosslinked monoliths in which the number of bonds formed exceeds the number of bonds broken under typically destructive mechanical conditions. The molecular-level modifications result in orders-of-magnitude increases in bulk moduli.

The ARM concept is shown in Fig. 1. The enabling chemistry is that of a mechanophore, a polymer-embedded mechanically reactive moiety. Much recent work has focused on using mechanophores and mechanochemistry^{6,7} to produce new chemistry^{8,9}, force accelerated and selective transformations^{10–21}, and stress-responsive material properties^{22–24}. The ARM polymers described within this paper incorporate large numbers of mechanophores

in the covalent structure of the polymer, so that the destructive forces responsible for bond scission also activate widespread latent reactivity in the mechanophores. We chose *gem*-dibromocyclopropanes (gDBC, **I_{closed}**) for the mechanophores embedded within a poly(butadiene) (PB) backbone (Fig. 1a) because the mechanically triggered ring opening leads to a 2,3-dibromoalkene product (**I_{open}**) that is susceptible to nucleophilic substitution¹⁴, which provides the basis for remodelling and potential self-strengthening or self-repair through covalent crosslinking, as proposed, but not demonstrated, elsewhere²⁵ (Fig. 1). The PB scaffold is attractive both synthetically and practically because of the ease of incorporating many mechanophores along a single polymer chain and its commercial utility. The parent gDBC mechanophore is inert towards nucleophilic substitutions, so the repair reaction only occurs when and where sufficient forces are experienced within the polymer to cause the non-scissile, ring-opening reactions.

We tested the ARM response to the shear forces of twin-screw extrusion, a common technique for bulk polymer processing. The conditions employed were destructive on a molecular level; extrusion of **I_{closed}** alone for 30 minutes at 40 °C and 50 revolutions per minute (r.p.m.) generated bulk shear stresses in the range 0.15–0.25 MPa (see Supplementary Information) that resulted in bond scission and a reduction in molecular weight from 780 to 560 kDa. At the same time, the shear forces responsible for chain scission mechanically activated the conversion of 7% of the gDBCs into their open form. Several pieces of evidence support a mechanical, rather than thermal, activation mechanism. Most compelling is to decouple the mechanophore from shear-generated tension along the polymer main chain by adding the gDBC to the pendant side-chain alkene of 1,2-PB. When 8 kDa, 66% 1,2-gDBC-PB polymer is co-extruded with 110 kDa *cis*-1,4-PB (40 minutes, 40 °C, 100 r.p.m.), the shear forces are large enough to degrade the molecular weight of the *cis*-1,4-PB to 68 kDa.

¹Department of Chemistry, Duke University, Durham, North Carolina 27708, USA, ²Weapons & Materials Research Directorate, Army Research Laboratory, Aberdeen Proving Ground, Aberdeen, Maryland 21005, USA, ³Department of Textile Engineering, Chemistry and Science, North Carolina State University, Raleigh, North Carolina 27695, USA. *e-mail: stephen.craig@duke.edu

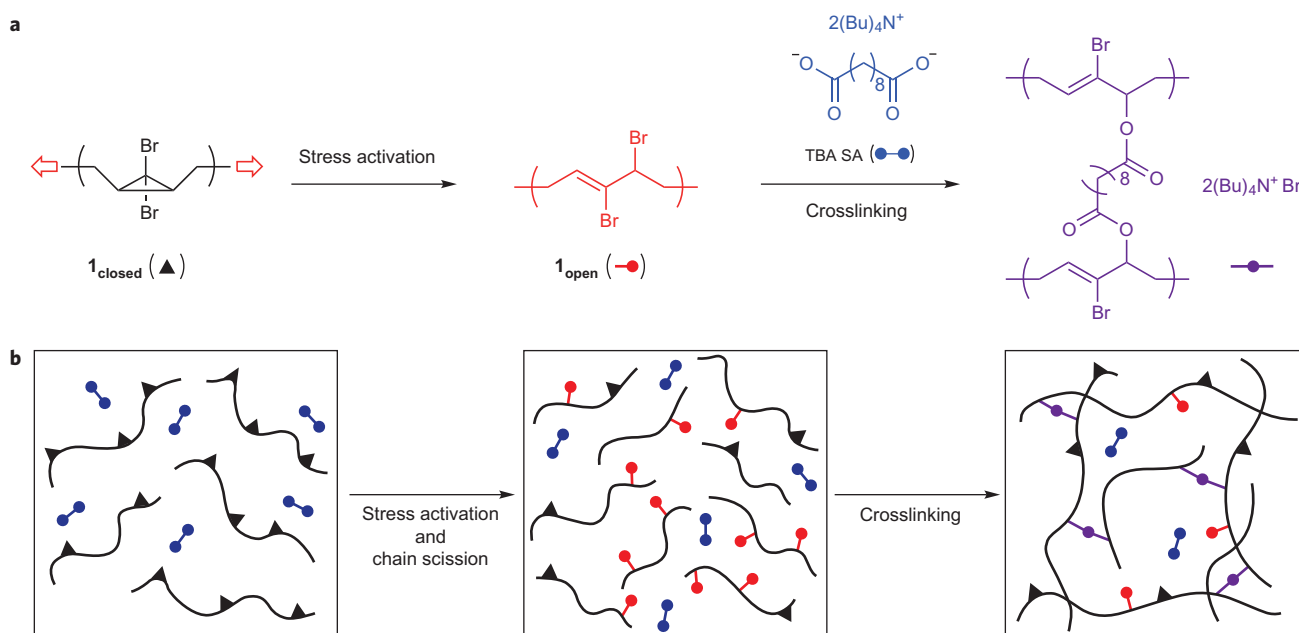


Figure 1 | The mechanochemical self-strengthening concept. **a**, A gDBC mechanophore within a polymer chain under tension undergoes a ring-opening reaction from $\mathbf{1}_{\text{closed}}$ to $\mathbf{1}_{\text{open}}$. This increases the contour length and provides an allylic bromide that is capable of self-strengthening through nucleophilic displacement reactions. **b**, System-wide force causes chain scission, but also activates the mechanophore (black triangle to red dot), which subsequently reacts with a crosslinker (blue) to form an active crosslink (purple) that overcomes the damage.

No activation was observed, however, in the 1,2-gDBC control sample, which supports a mechanical, rather than thermal, activation pathway (see Supplementary Information). Additional support is found in the increased activation previously reported to occur at lower extrusion temperatures¹⁴, and in the absence in the extruded sample of HBr elimination products from the ring-opened product that accompany the thermally activated reaction.

Reasoning that a divalent nucleophile might allow for polymer crosslinking, we extruded the **ARM-1** system, $\mathbf{1}_{\text{closed}}$, with the ditetrabutylammonium salt of sebacic acid (TBA SA; Fig. 2). We chose carboxylates as the nucleophiles because they are easily accessible and common functional groups in polymer chemistry, they show sufficient reactivity for nucleophilic substitution of the allyl bromide and, because of their weak basicity, they are not as prone to triggering elimination as other nucleophiles that we tested (for example, amines and alkoxides). The same shear conditions led to a solid polymer that, unlike extrusion of **1** alone, was insoluble in each of five different solvents and solvent combinations, consistent with the desired crosslinking. Interestingly, the mechanically triggered crosslinking appears to outcompete the destructive shear forces during the extrusion process, as the dynamic viscosity reading coupled to the extruder initially decreases, consistent with chain alignment and scission, but after ~ 13 minutes of extrusion, the required torque begins to increase slightly in a manner not observed in control polymers, which suggests an increase in molecular weight from crosslinking. Support for this crosslinking is provided by infrared spectroscopy, which reveals the disappearance of the TBA SA carboxylate stretch at $1,571\text{ cm}^{-1}$ and the appearance of a new carbonyl stretch at $1,721\text{ cm}^{-1}$ (Fig. 2), in excellent agreement with characteristic frequencies of esters and the value obtained in a model compound (see Supplementary Information).

This molecular-scale remodelling has a dramatic and positive impact on bulk mechanical properties. We characterized the properties of the samples using nanoindentation, which has emerged as a sophisticated and reliable technique for measuring the hardness and elastic modulus of materials at the submicron scale²⁶. Extruding $\mathbf{1}_{\text{closed}}$ led to insignificant changes in elastic modulus (8 ± 5 MPa for

$\mathbf{1}_{\text{closed}}$, 8 ± 3 MPa for $\mathbf{1}_{\text{open}}$), as determined by sampling each substrate at three different locations with four different loads, ranging from 30 to 60 μN . When the TBA SA salt was mixed with $\mathbf{1}_{\text{closed}}$ to form the **ARM-1** system, the modulus of the nascent sample reduced considerably (2 ± 0.5 MPa). When the **ARM-1** system was extruded, the remodelled sample that emerged was noticeably stiffer not only than in its unextruded form, but also than any of the other samples. Nanoindentation confirmed that the material became significantly stronger in response to typically destructive mechanical forces, with an increase of nearly two orders of magnitude in the elastic modulus to a value of 150 ± 85 MPa (see Supplementary Information). This increase is attributed primarily to the molecular-scale crosslinking that occurs in response to the mechanochemical trigger. Tetrabutylammonium bromide was formed by the crosslinking reaction, but its contribution to bulk material properties is assumed to be small and softening, comparable to the changes observed from the addition of TBA SA to $\mathbf{1}_{\text{closed}}$. In line with the interpretation of molecular-level self-strengthening, the modulus continues to increase in the resting, extruded sample as additional crosslinking reactions occur at the sites of mechanophore activation; by one week post-extrusion there was an increase in the infrared absorbance at $1,721\text{ cm}^{-1}$ (ester) and a concomitant decrease in absorbance at $1,560\text{ cm}^{-1}$ (free carboxylate). In that same time, the modulus nearly doubled to 280 ± 61 MPa. In comparison, $\mathbf{1}_{\text{closed}}$ and $\mathbf{1}_{\text{open}}$ registered modest or even negligible changes in modulus after a week (to 2 ± 1 MPa and 17 ± 9 MPa, respectively; see Supplementary Information).

We next tested the ARM concept in the context of shear-responsive polymer solutions. In solution, the mechanical triggers were elongational flow forces that accompany the collapse of cavitating bubbles during pulsed ultrasound^{27,28}. The resulting forces of tension along the backbone of polymer solutes of sufficient molecular weight (typically $>40\text{ kDa}$)²⁹ are quite large (nano-Newton range) and, as in the extrusion experiments, these forces are destructive and lead to chain scission and a decrease in polymer molecular weight. Larger molecular-weight polymers are more likely to experience forces necessary for scission, which makes them degrade

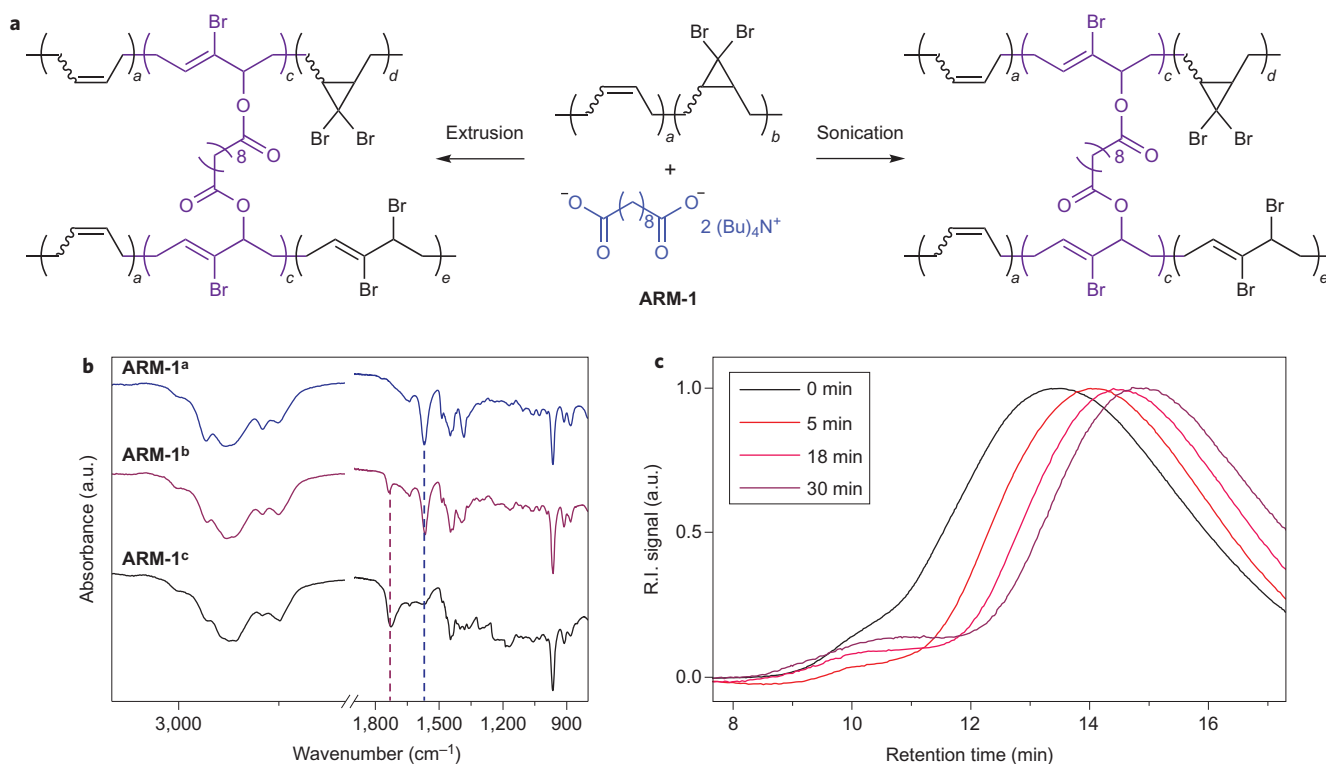


Figure 2 | Shear-induced mechanochemical crosslinking in solution and the bulk. **a**, The ARM-1 system responds to extrusion in the bulk (left) and sonochemical shearing in solution (right) by forming covalent crosslinks in the regions of high force along the polymer backbone. Polymer chain scission also occurs, but is not shown for clarity. The fraction of PB monomer (subscript *a* in the chemical formulae) remained constant throughout either experiment, and the fraction of gDBC mechanophore (*b*) decreases to (*d*) because of activation to the 2,3-dibromoalkene (*e*). A portion of the activated mechanophores reacts to form crosslinks (*c*). **b**, FTIR spectra overlay of the initial ARM-1 polymer (ARM-1^a, blue), the ARM-1 polymer extruded (ARM-1^b, purple) and the same ARM-1 polymer one week post-extrusion (ARM-1^c, black). The dotted lines designate the precursor carboxylate absorbance peak at 1,571 cm⁻¹ (blue) and the product ester absorbance peak at 1,721 cm⁻¹ (purple). **c**, Sonication of ARM-1 leads to fronting in the GPC trace, indicative of the early stages of network formation. a.u., arbitrary units.

faster³⁰, so we wondered whether the pace of bond making could match or exceed that of bond breaking.

We first explored the response of the ARM-1 two-component mixture used in the bulk studies. Monitoring the molecular weight of I_{closed} by gel permeation chromatography (GPC) as a function of sonication time in THF in the presence of TBA SA revealed the competition between the bond-breaking events that reduce molecular weight and the bond-forming events that increase molecular weight. As seen in Fig. 2, the GPC traces initially shift to longer retention times with increasing sonication, which indicates a decrease in polymer molecular weight and confirms that the high-shear environment is, indeed, destructive. At longer sonication times, however, a high molecular-weight front begins to grow into the chromatogram, indicative of early stages of gelation³¹, and sonication times in excess of 30 minutes result, first in the formation of insoluble precipitates and eventually in a free-standing film that can be peeled from the side of the Suslick vessel. As with the extrusion studies, these precipitates are insoluble in a wide variety of solvents.

To simplify the system, we engineered a single-component system (ARM-2) in which the crosslinking nucleophile is present on the same backbone as the mechanophore (Fig. 3). The activity of the mechanophore was demonstrated by subjecting precursor **2**, in which the carboxylic acid remains protonated and therefore unreactive to crosslinking, to pulsed ultrasound in the same manner as for I_{closed} , which again produced the desired 2,3-dibromoalkene. No precipitation or other evidence for intermolecular reactivity was observed as a consequence of sonicating **2**. When the carboxylic acid was activated to the nucleophilic carboxylate salt in ARM-2, however, sonication led to an even more prominent

precipitate formation than was observed in the two-component system. A newly formed infrared absorption peak at 1,724 cm⁻¹ again verified the formation of the desired ester crosslinks. The ARM response is efficient enough that bond making can outpace bond breaking during the pulsed ultrasound experiment, but an even more dramatic response ensues once the intermittent shear is stopped: the polymer solution gels to form an integrated, macroscopic crosslinked network. As in the bulk, mechanical-property measurements confirm the qualitative observations. The storage moduli of the various nascent polymer solutions, including unsonicated ARM-2, were at or below the limit of detection of our rheometer, whereas the stress-responsive gelation resulted in a modulus increase of greater than two orders of magnitude (see Supplementary Information). No increase in modulus was observed in sonicated polymer **2**, sonicated polymer **2**_{open} or unsonicated ARM-2 (Fig. 3). Fourier transform infrared spectroscopy (FTIR) again verified the formation of ester crosslinks, but at a greater relative population in the sample than in the two-component ARM system. As in previous cases, crosslinking was further confirmed by the insolubility of the dried gel in a wide variety of organic solvents.

The absence of gelation in nucleophilically inactive **2** provides good evidence that gelation does, indeed, require intermolecular crosslinking of the type proposed (the inactivity of the carboxylic acid in **2** is confirmed by an unchanged infrared absorbance at 1,700 cm⁻¹, which corresponds to the carboxylic acid rather than an ester), and this conclusion is further supported by additional observations (see Supplementary Information). First, if ARM-2 is sonicated at concentrations below its critical overlap concentration

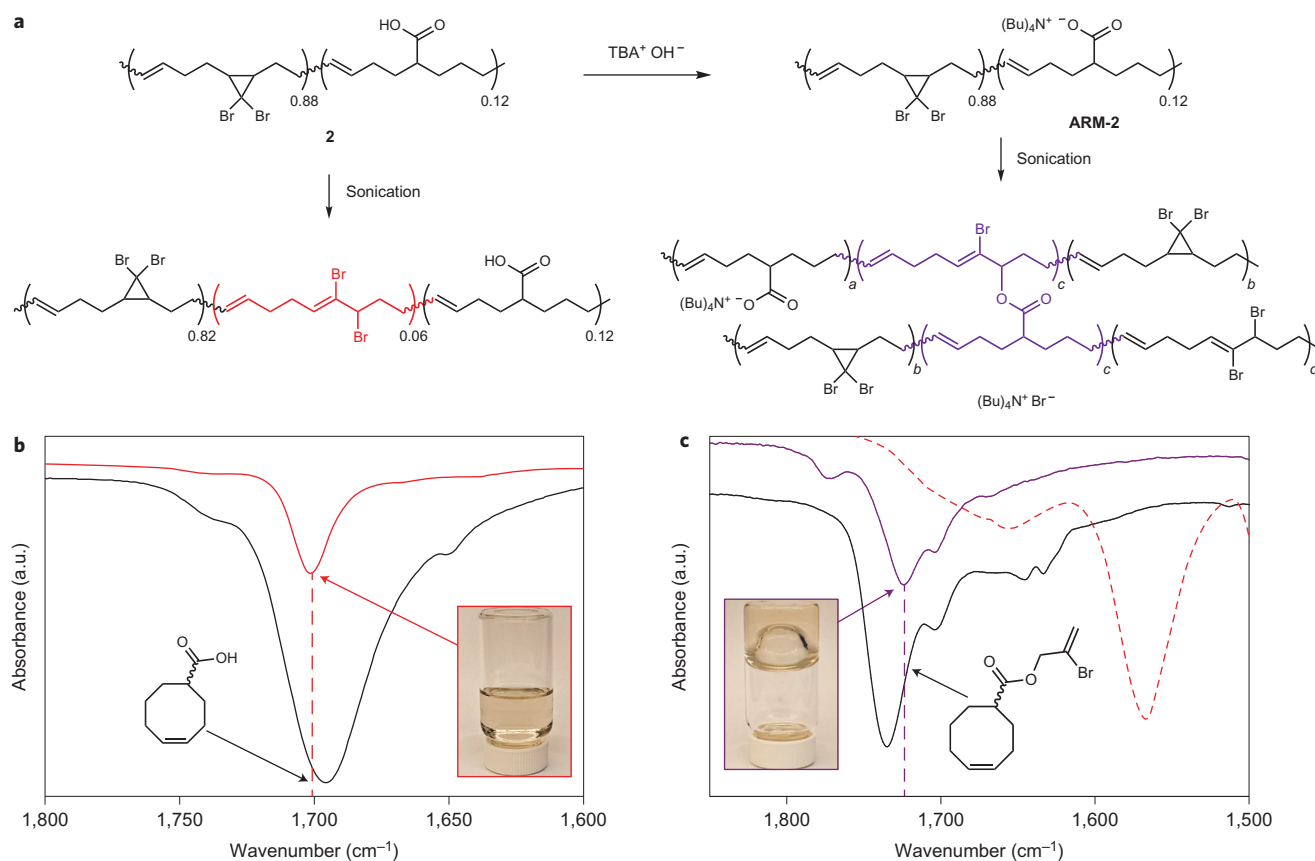


Figure 3 | Chemistry and response of a single-component ARM system. **a**, Treatment of **2** with $\text{TBA}^+ \text{OH}^-$ leads to the **ARM-2** system. Sonication of **2** leads to mechanochemical ring-opening of the mechanophore, but does not cause the carbonyl absorbance to shift from $1,701 \text{ cm}^{-1}$ in FTIR (**b**, red), which matches the model compound absorbance (**b**, black). Sonication of **ARM-2**, however, leads to covalent crosslinking and gelation through ester formation as indicated by the carbonyl absorbance at $1,724 \text{ cm}^{-1}$ (**c**, purple), in agreement with a small molecule model compound (**c**, black). Shown for contrast in **c** is the infrared spectrum of the TBA carboxylate of the model compound (dashed red line). Polymer main-chain scission also occurs in both cases, but is not shown for clarity.

(at which the average volume of a single polymer chain overlaps with the volume of another polymer chain, which favours intermolecular rather than intramolecular ester formation)³², no precipitates are formed during sonication and there is only a minimal increase in viscosity after the shear is stopped. Second, we showed previously that the *gem*-dichlorocyclopropane (gDCC) mechanophores are activated to the corresponding allyl chloride products to the same extent as the gDBC's under pulsed ultrasound, but small-molecule model systems demonstrate that, unlike the allylic bromide, the allylic chloride is not susceptible to nucleophilic displacement by a carboxylate. Consistent with expectations, sonication of the dichlorocyclopropanated polymer (**ARM-inactive**, see Supplementary Information) did not lead to precipitation, gelation or changes in the carbonyl region of the infrared spectrum. The same result was obtained with a polymer that contains only the carboxylate and no mechanophore. Third, sonication is necessary; allowing the **ARM-2** system to sit overnight without sonication results in no gelation. Fourth, the mechanical nature of the activation was confirmed by sonicating a low molecular-weight (9 kDa) **ARM-2** polymer, which experienced the same temperatures and pressures as the active **ARM-2** systems, but is below the limiting molecular weight for mechanical activation, and no ring opening or gelation was observed.

In the systems reported here, the consequences of molecular remodelling are global, in that the remodelling occurs throughout the material and they are observed in conjunction with irreversible deformation of the material (a characteristic of all reported bulk

mechanochemical activations of which we are aware). These results, however, also raise the intriguing possibility of localized mechanochemical self-strengthening to 'at-risk' regions within a load-bearing material, as occurs in biological systems. Localized remodelling should, therefore, be possible because the activation and subsequent crosslinking only occur at the discrete molecular sites that experience high forces of tension, and such molecular-scale forces are distributed to different extents in different classes of materials and loading environments, including crosslinked solids²². Whether local or global, orders-of-magnitude autonomous self-strengthening is shown here to be possible, and the magnitude of the response should be tunable through the nature of the mechanophore, its abundance within the material and the reactivity and concentration of the reacting partner. Underlying the response is a new principle for materials design, in which chemomechanical coupling is used to capture otherwise destructive mechanical energy and funnel it into constructive processes that, as in biological systems, actively remodel a synthetic material in response to its physical environment. The direct coupling of mechanical force to covalent chemistry differs from previously reported gelations triggered by sonication or shear^{33,34}, both in the mechanism of activation and in the controlled and potentially localized nature of the response. The same is true relative to conventional polymeric strain hardening caused by mesoscale morphological changes, such as polymer-chain alignment and/or crystallization³⁵. Finally, the use of polymer mechanochemistry makes available a rich palette of chemical responses, many of which are inaccessible via

thermal and/or photochemical stimuli, and so not only the mechanical but, ultimately, also the chemical, electronic or other functional properties of a material might be combined with the physical remodelling.

Methods

Preparation of ARM polymers. The synthesis, purification and characterization of all ARM polymers are described in detail in the Supplementary Information, including NMR, infrared and GPC data, mechanical characterization, control experiments and additional details.

Extrusion. Extrusion was performed on a Haake minilab microcompounder, comprising a clamshell barrel with two conical screws and a recirculation pathway to allow for extended processing intervals. The experiments were conducted using a recirculation pathway, which required about 7 ml of volume to allow for proper flow of the processed material. The polymer was introduced into the preheated barrel using a mechanical plunger, and the samples were processed at the indicated rate of screw rotation. Samples were stored under vacuum until ready to be processed. The compounder is equipped with two pressure transducers integrated in the backflow channel, which allows the measurement of sample dynamic viscosity. Pre- and post-extrusion moduli were characterized by nanoindentation, as described in the Supplementary Information.

Sonication. Ultrasound experiments (unless otherwise noted) were performed in BH-free THF (BHT = (3,5-di-*tert*-butyl-4-hydroxytoluene)) on a Vibracell Model VCX500 operated at 20 kHz with a 12.8 mm replaceable tip titanium probe from Sonics and Materials. Three-necked glass Suslick cells were obtained from Sonics and Materials and were oven dried before use. The sonications were carried out on 16 ml of the indicated solutions in THF in a room-temperature water bath. Solutions were degassed with bubbling N₂ for 30 minutes prior to sonication and a positive headspace of N₂ was kept during the experiment. Pulsed ultrasound was carried out at 8.7 W cm⁻² of power at one second on, six seconds off. Pre- and post-sonication moduli were characterized by rheometry, as described in the Supplementary Information.

Received 18 April 2013; accepted 27 June 2013;
published online 4 August 2013

References

- Odell, J. A. & Keller, A. Flow-induced chain fracture of isolated linear macromolecules in solution. *J. Polym. Sci. B* **24**, 1889–1916 (1986).
- Kudish, I. I., Airapetyan, R. G. & Covitch, M. J. Modeling of kinetics of stress-induced degradation of polymer additives in lubricants and viscosity loss. *Tribol. Trans.* **46**, 1–10 (2003).
- Zhurkov, S. N. & Korsukov, V. E. Atomic mechanism of fracture of solid polymers. *J. Polym. Sci. B* **12**, 385–398 (1974).
- Keckes, J. *et al.* Cell-wall recovery after irreversible deformation of wood. *Nature Mater.* **2**, 810–814 (2003).
- Watson, G. M. & Mire, P. Reorganization of actin during repair of hair bundle mechanoreceptors. *J. Neurocytol.* **30**, 895–906 (2001).
- Caruso, M. M. *et al.* Mechanically-induced chemical changes in polymeric materials. *Chem. Rev.* **109**, 5755–5798 (2009).
- Black, A. L., Lenhardt, J. M. & Craig, S. L. From molecular mechanochemistry to stress-responsive materials. *J. Mater. Chem.* **21**, 1655–1663 (2011).
- Hickenboth, C. R. *et al.* Biasing reaction pathways with mechanical force. *Nature* **446**, 423–427 (2007).
- Lenhardt, J. M. *et al.* Trapping a diradical transition state by mechanochemical polymer extension. *Science* **329**, 1057–1060 (2010).
- 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.* **132**, 15936–15938 (2010).
- Park, I. & Sheiko, S. S. Molecular tensile testing machines: breaking a specific covalent bond by adsorption-induced tension in brushlike macromolecules. *Macromolecules* **42**, 1805–1807 (2009).
- Wiita, A. P., Ainavarapu, S. R. K., Huang, H. H. & Fernandez, J. M. Force-dependent chemical kinetics of disulfide bond reduction observed with single-molecule techniques. *Proc. Natl Acad. Sci. USA* **103**, 7222–7227 (2006).
- Brantley, J. N., Wiggins, K. M. & Bielawski, C. W. Unclicking the click: mechanically facilitated 1,3-dipolar cycloreversions. *Science* **333**, 1606–1609 (2011).
- Black, A. L., Orlicki, J. A. & Craig, S. L. Mechanochemically triggered bond formation in solid-state polymers. *J. Mater. Chem.* **21**, 8460–8465 (2011).
- Berkowski, K. L., Potisek, S. L., Hickenboth, C. R. & Moore, J. S. Ultrasound-induced site-specific cleavage of azo-functionalized poly(ethylene glycol). *Macromolecules* **38**, 8975–8978 (2005).
- Karthikeyan, S., Potisek, S. L., Piermattei, A. & Sijbesma, R. P. Highly efficient mechanochemical scission of silver–carbene coordination polymers. *J. Am. Chem. Soc.* **130**, 14968–14969 (2008).
- Kryger, M. J. *et al.* Masked cyanoacrylates unveiled by mechanical force. *J. Am. Chem. Soc.* **132**, 4558–4559 (2010).
- Paulusse, J. M. J. & Sijbesma, R. P. Reversible mechanochemistry of a Pd(II) coordination polymer. *Angew. Chem. Int. Ed.* **43**, 4460–4462 (2004).
- Yang, Q.-Z. *et al.* A molecular force probe. *Nature Nanotech.* **4**, 302–306 (2009).
- Klukovich, H. M. *et al.* Tension trapping of carbonyl ylides facilitated by a change in polymer backbone. *J. Am. Chem. Soc.* **134**, 9577–9580 (2012).
- Klukovich, H. M., Kouznetsova, T. B., Kean, Z. S., Lenhardt, J. M. & Craig, S. L. A backbone lever-arm effect enhances polymer mechanochemistry. *Nature Chem.* **5**, 110–114 (2013).
- Davis, D. A. *et al.* Force-induced activation of covalent bonds in mechanoresponsive polymeric materials. *Nature* **459**, 68–71 (2009).
- Crenshaw, B. R. *et al.* Deformation induced color changes in mechanochromic polyethylene blends. *Macromolecules* **40**, 2400–2408 (2007).
- Chen, Y. *et al.* Mechanically induced chemiluminescence from polymers incorporating a 1,2-dioxetane unit in the main chain. *Nature Chem.* **4**, 559–562 (2012).
- Kean, Z. S. & Craig, S. L. Mechanochemical remodeling of synthetic polymers. *Polymer* **53**, 1035–1048 (2012).
- Oliver, W. C. & Pharr, G. M. An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. *J. Mater. Res.* **7**, 1564–1583 (1992).
- Paulusse, J. M. J. & Sijbesma, R. P. Ultrasound in polymer chemistry: revival of an established technique. *J. Polym. Sci. Polym. Chem.* **44**, 5445–5453 (2006).
- May, P. A. & Moore, J. S. Polymer mechanochemistry: techniques to generate molecular force via elongational flows. *Chem. Soc. Rev.* <http://dx.doi.org/10.1039/c2cs35463b> (2013).
- Basedow, A. M. & Ebert, K. H. in *Advances in Polymer Science* Vol. 22 (eds Cantow, H.-J. *et al.*) 83–148 (Springer, 1977).
- Nguyen, T. Q., Liang, Q. Z. & Kausch, H. H. Kinetics of ultrasonic and transient elongational flow degradation: a comparative study. *Polymer* **38**, 3783–3793 (1997).
- Schosseler, F., Benoit, H., Grubisic-Gallot, Z., Strazielle, C. & Leibler, L. Gelation process by size-exclusion chromatography coupled with light scattering. *Macromolecules* **22**, 400–410 (1989).
- Francis, R. S., Patterson, G. D. & Kim, S. H. Liquid-like structure of polymer solutions near the overlap concentration. *J. Polym. Sci. Polym. Phys.* **44**, 703–710 (2005).
- Naota, T. & Koori, H. Molecules that assemble by sound: an application to the instant gelation of stable organic fluids. *J. Am. Chem. Soc.* **127**, 9324–9325 (2005).
- Carnall, J. M. A. *et al.* Mechanosensitive self-replication driven by self-organization. *Science* **327**, 1502–1506 (2010).
- Carey, B. J., Patra, P. K., Ci, L., Silva, G. G. & Ajayan, P. M. Observation of dynamic strain hardening in polymer nanocomposites. *ACS Nano* **5**, 2715–2722 (2011).

Acknowledgements

This material is based on work supported by the US Army Research Laboratory and the Army Research Office under Grant W911NF-07-1-0409 and the National Science Foundation (DMR-1122483). A.L.B.R. was supported by a Department of Defense Science, Mathematics and Research for Transformation Fellowship and Z.S.K. by a National Institutes of Health NIGMS Biotechnology Predoctoral Training Grant (T32GM8555).

Author contributions

A.L.B.R. and S.L.C. conceived and designed the experiments. A.L.B.R. and Z.S.K. performed the synthesis, J.A.O. contributed extrusion equipment and analysed that data with A.L.B.R. A.L.B.R. and S.M.E. performed the shear experiments. W.E.K. contributed the nanoindentation tools and M.C. performed the nanoindentation experiments and analysed that data. A.L.B.R., Z.S.K. and S.L.C. analysed the data and co-wrote the paper.

Additional information

Supplementary information is available in the [online version](#) of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to S.L.C.

Competing financial interests

The authors declare no competing financial interests.