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gem-Dichlorocyclopropanes as Abundant and Efficient Mechanophores in Polybutadiene Copolymers under Mechanical Stress

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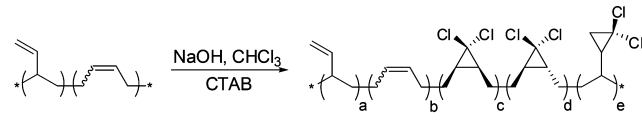
There is rapidly escalating interest in the synthesis and characterization of latent reagents[1] and catalysts[2] that undergo mechanically initiated activation when coupled to a directional restoring force. The construction and characterization of novel mechanophores might advance the fundamental understanding of how mechanical force directs chemical reactivity[3,4] and provide access to new stress-responsive materials, such as polymers that strengthen or repair autonomously at the molecular level. Seminal work by Hickenboth et al.[1] has shown that a single benzocyclobutene (BCB) incorporated near the center of polymers can be mechanically activated to undergo ring opening, resulting in a reactive *o*-quinodimethine without polymer chain scission. The BCB studies and related work with spiropyran-centered polymers[5] represent important steps toward in situ mechanochemistry for stress-responsive polymers.

In many cases, it would be desirable to disperse mechanophores at high density throughout a polymer matrix so the precise region(s) of high stress need not be predicted in advance. The activity of multiple, nonscissile mechanophores in a single polymer chain, however, has yet to be demonstrated. Here we report that *gem*-dichlorocyclopropanes (*g*DCCs) undergo mechanically assisted ring-opening reactions when coupled to ultrasound-generated elongational shear flows and that several hundreds of these reactions occur on the time scale of a single polymer chain scission, providing a "mechanochemical map" of the stress distributions. The ability to easily synthesize copolymers of these newly identified mechanophores allows their relative activities to be evaluated as a function of the stereo- and regiochemistry by which they are coupled to the strain field. The reactivity patterns suggest that multiple mechanically assisted reactions occur not only in a single polymer chain but also during a single elongational strain event.

The *g*DCCs were incorporated along the backbone of *cis*-polybutadiene (PB, **1**) (156 kDa) by its reaction with aqueous NaOH in $CHCl_3$ under phase-transfer conditions,[6] resulting in *g*DCC−PB copolymer **2** (310 kDa) (Figure 1). The copolymer was then subjected to pulsed ultrasound in THF at 6−9 °C under a nitrogen atmosphere. Aliquots were removed periodically, and the subsequent ring opening was monitored by ^{1}H and ^{13}C NMR spectroscopy, while the covalent-bond scission frequency was determined from the change in number-average molecular weight (M_N) by gel permeation chromatography (GPC) and multiangle light scattering (MALS).

As a result of a combination of angular and bond-lengthening changes in geometry, appropriately coupled electrocyclic processes, such as ring openings of BCB and *g*DCC, are especially susceptible to mechanical activation.[4] Sonication of copolymer **2** in THF leads to significant changes in both its ^{1}H and ^{13}C spectra. Most telling are new ^{1}H resonances at 5.86 and 4.46 ppm, as well as a significant loss of intensity from the *g*DCC ring protons at 1.6 ppm, coincident with the formation of new resonances in the methylene region between 2.4 and 1.9 ppm. These chemical shifts are consistent with



Sample	M_N (kDa)	a	b	c	d	e
1	156	0.02	0.98	----	----	----
2	310	0.02	0.26	0.72	----	----
3	241	0.09	0.19	0.35	0.37	----
4	167	0.72	----	0.05**		0.23
5	6.5	----	0.62	0.38**		----

Figure 1. *g*DCC-PB copolymers with fractional monomer contents a−e. Entries labeled ** are sums of *cis*- and *trans*-*g*DCC units, and ---- indicates that no ^{1}H NMR resonance was detected.

the formation of 2,3-dichloroalkenes (Figure 2), which are well-known products of electrocyclic *g*DCC ring openings, as opposed to reactions that proceed through diradical intermediates via potential homolytic bond scission.[7] Corroborating evidence comes from ^{13}C resonances, COSY cross-peaks, and IR spectroscopy [see the Supporting Information (SI)]. By comparison, sonication of unfunctionalized **1** leads to no change in the relative intensities or chemical shifts of the ^{1}H resonances. The extent of ring opening was determined from integrations of the ^{1}H NMR resonances of the 2,3-dichloroalkene at 5.86 and 4.46 ppm relative to that of the PB alkene at 5.4 ppm, whose intensity remains constant over the course of the reaction. A series of observations support the conclusion that the ultrasound-induced reactivity is dominated by mechanical contributions. First, the extent of *g*DCC ring opening is well-correlated with that of chain scission (Figure 3), the mechanical origin of which is generally accepted.[8] Second, the 6.5

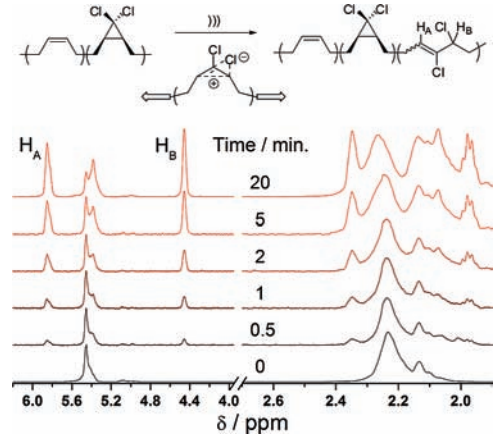


Figure 2. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of aliquots taken from sonochemical degradation of polymer **2** (THF, 6−9 °C, N_2 atmosphere). New resonances from the 2,3-dichloroalkene product are denoted H_A and H_B. The 1,4-PB resonance at ∼5.4 ppm shifts slightly as proximal 2,3-dichloroalkenes are formed. The net electrocyclic process is shown below the reaction arrow; both one- and two-step reactions are possible.[7]

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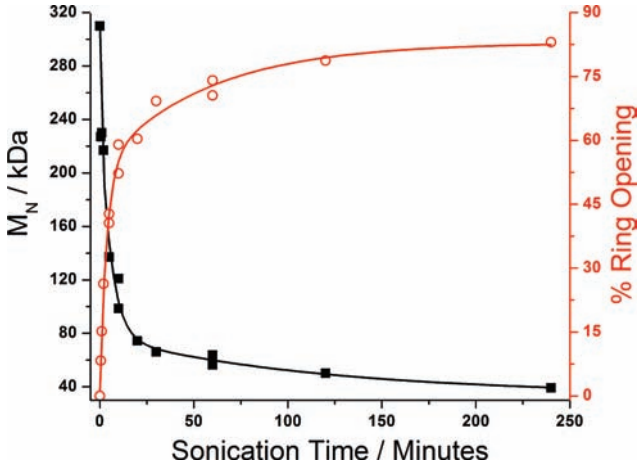

Figure 3. Sonication of polymer **2** (1 mg/mL in THF, 6−9 °C, N_2 atmosphere) leads to ring-opened 2,3-dichloroalkenes (○) with simultaneous degradation of the polymer molecular weight (■).

kDa polymer **5** is below the critical molecular weight necessary to experience significant elongational shear forces, and identical sonication conditions produce no evidence of ring opening.

Though these controls are generally accepted indicators of mechanical assistance, similar studies have been questioned.[9] We therefore decoupled the *g*DCC units from the mechanical restoring force by forming them on the side-chain alkenes of 1,2-PB to give **4**. We observed no evidence for reaction of these side-chain functional groups under polymer shear stresses that open >50% of the main-chain *g*DCCs, confirming a mechanical rather than thermal origin in the induced reactivity (see the SI).

The *g*DCC ring opening is orders of magnitude faster under shear than is chain scission, leading to significant mechanochemical remodeling of the polymer backbone. For **2** (310 kDa by MALS), an average of one scission per polymer (halving of M_N) occurs after ∼4.5 min of sonication, by which point 35% of the *g*DCC units have been forced open (an average of ∼690 per chain). When **2** is sheared for 4 h, over 80% of the *g*DCC rings open, while the molecular weight degrades from 310 to 39 kDa; this corresponds to an average of 1650 ring openings and 3 chain scission cycles, or ∼7 breaks per original polymer.

The relative reactivity of differentially coupled mechanophores provides insights into the reaction dynamics. Polymer **3** contains roughly equal fractions of *cis*- and *trans*-*g*DCC units (35 and 37%, respectively) that must experience, on average, the same shear forces during the sonication. Under stress-free conditions, the cis isomers react ∼20× faster than the trans ones.[10] We expected the mechanically assisted rates to differ by an even greater extent because the symmetry-allowed disrotatory ring openings of *cis*-*g*DCC should be better coupled to the restoring force than those of the trans isomer.[1,4c] Surprisingly, analysis of ^{1}H NMR spectra (see the SI) indicates that the reaction probabilities are nearly equivalent: only 1.35 ± 0.22 *cis*-*g*DCCs react for every *trans*-*g*DCC. Interestingly, this (lack of) selectivity is comparable to that reported earlier for BCB mechanophores, *even though the reaction symmetry rules are opposite*. The muted selectivity suggests that the elongational shear dynamics create fairly localized regions of very high stress along the main polymer chain, in which a high percentage of *g*DCCs react during a single chain-scission event regardless of their stereochemistry. These results are consistent with the known difficulty of programming chemoselectivity into ultrasound-induced bond scissions,[11] although interesting reaction dynamics might also contribute.[4c]

In conclusion, dichlorocyclopropanation provides easy access to multigram quantities of mechanically active copolymers. Shear-induced *g*DCC ring opening occurs several hundred times more often than chain scission, but only when the elongational force is coupled directly to the expected reaction coordinate. The vigorous mechanical activity indicates that multiple chemical responses can be triggered during a single, short strain event, potentially with positional precision comparable to the size of a monomer unit (subnanometer). The large population of mechanophores provides a probe of molecular stress distributions along the polymer chains during ultrasonication, a methodology that might be extended to other load-bearing environments. The extensive and efficient mechanochemical remodeling further suggests new sonochemical strategies for postsynthetic modification that are orthogonal to conventional methods, inspiring the pursuit of additional, scalable mechanophores for that purpose. Because stress-free *g*DCCs are not intrinsically very reactive,[10] we anticipate that a rich toolkit of mechanically induced chemistry will rapidly be developed.

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Supporting Information Available: Details of syntheses, characterization, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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