Dynamic Memory Effects in the Mechanochemistry of Cyclic Polymers

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Supporting Information Placeholder

ABSTRACT: Cyclic polymers containing multiple *gem*-dichlorocyclopropane (*g*DCC) mechanophores along their backbone were prepared using ring expansion metathesis polymerization (REMP). The mechanochemistry of the cyclic polymers was investigated using pulsed ultrasonication. The fraction of *g*DCC mechanophores that are activated per chain halving event (Φ) was compared to that of linear analogs. For 167 kDa cyclic polymer, Φ = 0.38, vs. Φ = 0.62 for 158 kDa for linear polymers analogs, even though cyclic chain fragmentation necessarily proceeds through a linear intermediate of comparable composition to the initially linear systems. Ozonolysis of the mechanochemical products further shows that the mechanochemical "activation zone" in the cyclic polymer is less continuous than in the linear polymer. These results suggest that the linear intermediate in cyclic polymer fragmentation undergoes subsequent scission during the same high strain rate extensional event in which it is formed and furthermore retains at least a partial memory of its original cyclic conformation at the time of fragmentation.

Progress in covalent polymer mechanochemistry has revealed a range of fundamental insights into the dynamics of mechanically coupled chemical reactions. Force-coupled kinetics and dynamics within mechanophores has received considerable attention, with insights into stereochemical,[1-6] regiochemical,[7-12] and substituent[13-14] effects, including the impact of mechanical bonds[15-16] on mechanophore activation, mechanically accelerated and suppressed chemical reactions,[17-18] and force stabilized maleimide–thiol adducts.[19] Studies of the influence of polymer chain structure have disclosed the interplay of scissile and non-scissile events,[20] the impact of chain branching in star[21] and bottlebrush[22] architectures, and the influence of micellar assembly.[23-24] Recently, Diesendruck[25] has shown that collapsing a single linear chain into a cross-linked nanoparticle enhances shear resistance, while Peterson and co-workers[26] reported multiple ruptures of denpols in a single extension event. The single chain dynamics in question arise in the context of high strain rate extensional strains, such as those generated by pulsed ultrasonication, in which the polymer experiences a peak force near its midpoint. We wondered about the consequences of removing a fixed midpoint, specifically by embedding mechanophores in a cyclic polymer.

The mechanochemistry of cyclic polymers has been considered previously,[27] but to the best of our knowledge there is only a single experimental report on the subject, in which Moore and Boydston showed that sonomechanical scission of self-immolative cyclic poly(phthalaldehyde) triggered a cascade depolymerization to *o*-phthalaldehyde monomer.[28] Dynamics specific to the cyclic architecture were not addressed. Cyclic polymers (other than self-immolative ones) differ from linear analogs in that initial chain scission does not reduce molecular weight; fragmentation requires a second chain scission event (Figure 1). Moreover, the evolution of strain in cyclic polymers likely differs from that in linear polymers.[29] Here, we report the mechanochemistry of cyclic polymers with multiple non-scissile mechanophores embedded along the polymer backbone. Comparison to linear analogs suggests conformational memory effects in high strain rate extensional flow fields.

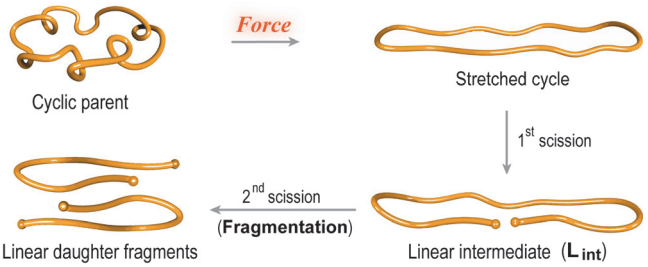
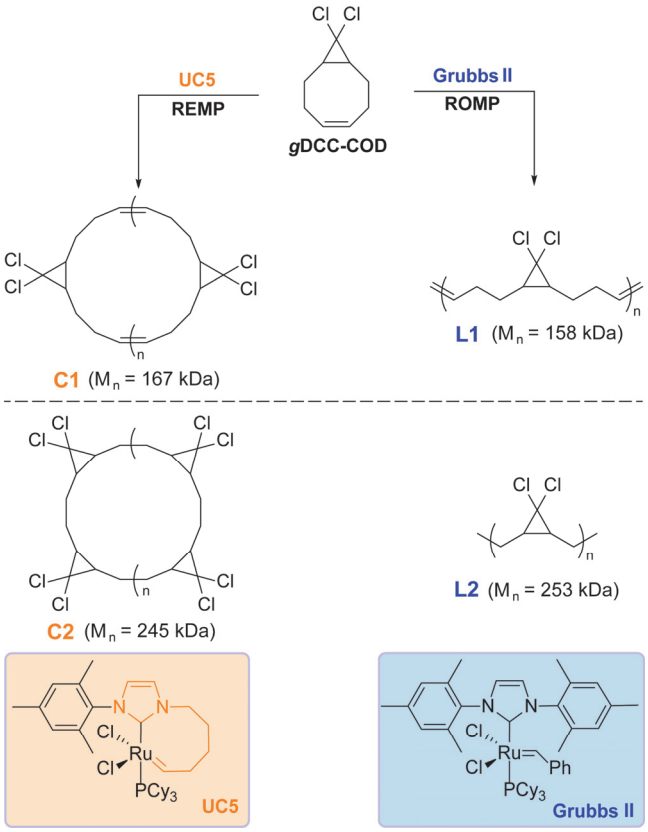


Figure 1. Depiction of mechanical scission of a cyclic polymer to give a linear intermediate that subsequently fragments into two linear daughter polymers

From the synthetic strategies available to prepare cyclic polymers,[30-31] we chose cyclic ruthenium-alkylidene catalyzed ring expansion metathesis polymerization (REMP), which has been used to produce cyclic polymers (Scheme 1) with high molecular weight and purity[32-34] and, unlike other techniques,[35] is readily compatible with previous cyclooctene-based mechanophore monomers. Catalyst UC5 was selected for REMP because its favorable catalyst releasing process[36-37] minimizes residual ruthenium complexes on the polymer backbone that may serve as weak bonds in the chain.[38] A representative REMP of *gem*-dichlorocyclopropanated cyclooctadiene (gDCC-COD) at 40 °C for 12 h gave polybutadiene-based gDCC polymer (**C1**, M_n = 167 kDa). For comparison, linear polymer **L1** (M_n = 158 kDa) was prepared *via* ring opening metathesis polymerization (ROMP) using Grubbs II catalyst (Scheme 1).[39] **C1** has a lower intrinsic viscosity (M_n = 154 kDa, [η] = 0.098 mL/mg) than **L1** (M_n = 141 kDa, [η] = 0.108 mL/mg), as expected of a cyclic polymers (see Figures S1 and S2, Supporting Information). We of course cannot rule out the possible presence of linear impurities in **C1**, but any such impurities would mean that the differences in behavior observed here underreport, if anything, the true differences in these two topologies.

Scheme 1. Top: synthesis of cyclic and linear polymers; Bottom: catalysts and other polymers used in this study.



Solutions (2 mg/mL, THF) of **C1** and **L1** were subjected to pulsed ultrasonication (8.7 W/cm^2, 0 °C, 1s on/1s off, N_2) to assess the competition between two mechanochemical responses: the non-scissile ring opening of *g*DCC to 2,3-dichloroalkene, and the fragmentation of the parent polymers to daughter fragments through one (linear) or two (cyclic) chain scission events. In both cases, fragmentation into daughter polymers of lower M_n is observed: from 167 to 90 kDa for **C1** and 158 kDa to 103 kDa **L1** after 20 min. At the same time, *g*DCC mechanophores along the backbone react in response to the force along the polymer (Figure 2b).

Figure 3 shows the extent of *g*DCC ring opening (quantified by ^{1}H NMR) as a function of what we have defined previously as scission cycle, although here we refer to it as fragmentation cycle (FC, eq 1), since the first scission event of a cyclic polymer does not reduce molecular weight.

$$FC = \frac{\ln M_{n(0)} - \ln M_n}{\ln 2} \qquad (1)$$

In eq. 1, $M_{n(0)}$ and M_n are initial and sonicated number-average molecular weight (GPC-MALS), respectively. The competition between *g*DCC ring opening and fragmentation can be quantified by the slope Φ of the plot of ring opening vs. FC.[40]

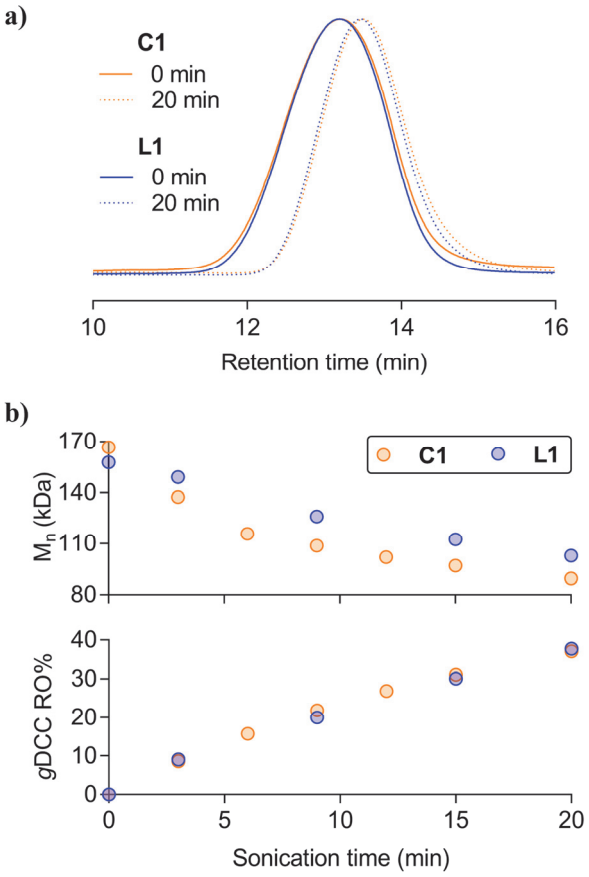


Figure 2. a) Normalized GPC traces of **C1** (orange) and **L1** (blue) as a function of sonication time. b) Evolution of M_n (top) and *g*DCC ring opening (bottom) with sonication time.

We anticipated a greater extent of ring opening with fragmentation in **C1** than **L1** for three reasons. First, fragmentation of **C1** requires two scission events in which the tension is focused in two different regions of the polymer, whereas only a single region of tension focusing is required for the fragmentation of **L1**. Second, if there were substantial *g*DCC ring opening without scission, subsequent stretching events in **L1** should focus tension in the same middle portion of the polymer where *g*DCCs have already been activated, whereas subsequent stretching of **C1** would likely focus tension on a different set of unopened *g*DCC mechanophores. Third, and most significantly, the fragmentation of **C1** proceeds through a linear intermediate (**L$_{int}$**) (Figure 1) that is effectively chemically identical to **L1**, and so the total *g*DCC activation observed following its subsequent scission was expected to be at least that observed in **L1**, plus any non-overlapping *g*DCCs that were activated in the first **C1**-to-**L$_{int}$** scission event.

Remarkably, the opposite is observed: less *g*DCC ring opening occurs per **C1** fragmentation (Φ = 0.38) than **L1** fragmentation (Φ = 0.62). This observation cannot be ascribed to possibly lower forces acting on the cyclic polymer, because the use of FC means that we are comparing *g*DCC activation alongside stretching events at which the force necessary to induce bond scission is reached.[20] Because **C1** and **L1** have the same composition along their backbone, we are comparing *g*DCC activation relative to events that reach on average the same peak force.

Another potential explanation is that residual catalyst in **C1** might be responsible, by creating a "weak link" along the polymer backbone.[38] ICP-MS analysis, however, quantifies the residual ruthenium in **C1** to be 166 ppm (similar to previous reports[37]), or 0.27 mol UC5 per mol **C1** (see ESI). Even if all of the residual Ru is

contained in the polymer main chain (unlikely, since UC5 favors a released state[36-37] that limits residual main-chain ruthenium-carbene bonds) and if **C1** with UC5 fragmented without any accompanying *g*DCC ring opening, the remaining **C1** would have a Φ value of 0.52 (0.38/0.73), which is still less than that of **L1** (Φ = 0.62). Similar values are found in 98 kDa **C1** with residual ruthenium of 130 ppm (0.13 Ru per polymer), for which Φ = 0.44 vs. Φ = 0.70 for 94 kDa **L1** (see Supporting Information). Finally, the fragmentation of **C1** requires two scissions, and the fraction of polymer chains with two or more embedded UC5 is negligible relative to the magnitude of the effects observed.

We conclude, therefore, that $\mathbf{L}_{int}$ formed *via* initial **C1** scission is not identical to **L1**. As $\mathbf{L}_{int}$ and **L1** are structurally indistinguishable (except for any prior ring-opened *g*DCC in $\mathbf{L}_{int}$), their differences are likely a consequence of their conformational history. In other words, $\mathbf{L}_{int}$ retains a "memory" that it was formed *via* **C1** scission, and that memory persists (on average) through its subsequent scission/fragmentation.

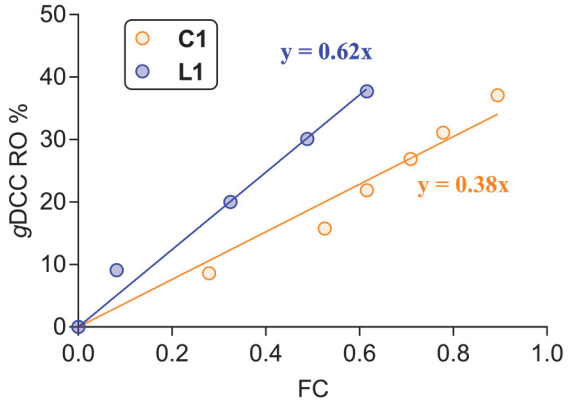


Figure 3. *g*DCC ring opening as a function of fragmentation cycle (FC) for **C1** and **L1** polymers in this study. Solid lines are linear fits through the origin; slope = Φ.

Any conformational memory would disappear rapidly once the polymer relaxes, and so we conclude that fragmentation of $\mathbf{L}_{int}$ occurs in the same extension event as initial scission. Further support for single-event fragmentation is provided by radical trapping experiments (Figure S10). Trapped in the high strain flow field, $\mathbf{L}_{int}$ could fragment before it can fully extend from its as-formed pseudo-cyclized conformation. Metastable, partially coiled intermediates in chain extension have been observed by Chu and coworkers in the extensional unwinding of DNA,[41] but to the best of our knowledge evidence for similar conformational dynamics in the sonication of synthetic polymers has yet to be reported.

As tension is distributed differently during **C1** fragmentation relative to that in **L1**, we sought other manifestations of that distribution. We have observed previously that the activation of non-scissile *g*DCC mechanophores in linear poly(*g*DCC) occurs in nearly perfect blocks along the polymer main chain.[42] We performed dichlorocyclopropanation of **L1** to give polymer **L2** (M_n = 253 kDa) with no detectable backbone alkenes. Subsequent sonication gave daughter fragments of M_n = 122 kDa with 56% *g*DCC repeats ring-opened to 2,3-dichloroalkenes, while 44% (accounting for on average 57 kDa per chain) remain unreacted. Further ozonolysis cleaves all alkenes, and leaves pure (by ^{1}H NMR, Figure S18) poly(*g*DCC) of M_n = 60 kDa (Table 1). In other words, the unactivated *g*DCCs are almost entirely continuous, consistent with our previous observations. Similar treatment of **C2** (M_n = 245 kDa, prepared from dichlorocyclopropanation of **C1**), however, produced different results. For **C2**, daughter fragments were produced with M_n = 122 kDa and 60% (73 kDa) of unreacted *g*DCC repeats per chain, but ozonolysis produced pure poly(*g*DCC) polymer of only M_n = 41 kDa. The fragmentation of **C2** involves the production of (on average) more than one region of *g*DCC ring opening per daughter. A reasonable possibility would be two different regions, each extending from one of the two sites of scission.

The sonication of a cyclic polymer leads to an initial increase in tension and resultant chain scission event. The data presented here suggest that cyclic polymer fragmentation through a second scission rapidly follows the initial scission during the same extensional event, and the increased tension and second scission event occur in positions that are remote to the first scission. Prior to this second scission, the linear intermediate of the primary cyclic scission does not explore the same conformational space available to nascent linear polymers during identical sonication conditions – with at least one end presumably remaining partially "folded" back toward itself. Such restricted dynamics are reasonable, given that the strain rates necessary to extend the polymer to the point of its first break must exceed the rates of conformational relaxation (else the chain would relax before extending and breaking).[43-44] We note that the extreme limit of this dynamic conformational trapping would be an extremely short lifetime for $\mathbf{L}_{int}$, to the extent that the two scission events might be considered effectively simultaneous.

This picture suggests the potential importance of conformational dynamics in the very high strain rate environment of pulsed ultrasonication, which exceed those employed in previous studies of cyclic polymers.[45-48] The consequences of such dynamics might be exaggerated here due to the initial pseudo-cyclic conformation of $\mathbf{L}_{int}$, but these results raise the possibility that conformations that are similarly "trapped" during high strain rate processes[41] might also play a role in the mechanochemistry of linear polymers. Furthermore, these results suggest the intriguing possibility of conformational memory effects in other high strain rate processes, such as the propagation of shock waves in polymeric materials.[49] Cyclic and other topologically complex polymers might therefore provide potential opportunities to tune mechanochemical response in bulk materials as well as sonochemical environments. The role of such architectures and influence of (for example) molecular weight, chain stiffness, and solvent quality on dynamic behavior seems to us to be a promising area for further inquiry.

ASSOCIATED CONTENT

Supporting Information. Synthetic procedures, characterizations, and mathematical analysis. The Supporting Information is available free of charge on the ACS Publications website.

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Notes

The authors declare no competing financial interest.

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Table 1. Effect of sonication and subsequent ozonolysis on L2 and C2 homopolymers

Polymer	M_n (kDa)	Post-sonication					Post-ozonolysis	
		Time (min)	M_n (kDa)	*Đ*	*g*DCC ring opening%	*g*DCC/chain (kDa)	M_n (kDa)	*Đ*
L2	253	10	122	1.37	56%	57	60	1.61
C2	245	12	122	1.31	40%	73	41	1.62

TOC