Characterizing the mechanochemically active domains in *gem*-dihalocyclopropanated polybutadiene under compression and tension†

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The incorporation of mechanically active functional groups, or mechanophores, along polymer backbones offers opportunities for new stress-responsive material properties and also provides a method by which to probe fundamental questions related to molecular stress distributions in polymeric materials under load. The activation of covalent chemistry in polymers has primarily been demonstrated in solution, but to date little is known regarding activation in the solid state. In the latter regard, recent effort has focused on the use of spectroscopically active mechanophores that directly probe the presence of stress within materials. The distribution of forces within individual polymer chains, however, has yet to be characterized. Herein we report that *gem*-dihalocyclopropane (gDHC) functionalized polybutadiene is mechanochemically active in the solid state, and that the strain-triggered ring opening of the gDHCs provides quantitative information regarding the number of mechanically active monomers and the size of the mechanically activated domains along individual polymer backbones within bulk materials subjected to compressive and tensile loads. The results show that high mechanical forces are concentrated over lengths of only a few monomers.

1 Introduction

There is increasing interest in the design and synthesis of mechanically activated, polymeric materials. This area of research, polymer mechanochemistry, focuses on the directed chemical reactions of polymer-embedded reactive moieties, or mechanophores, as a result of a coupled restoring force along the polymer chain. Notable successes of mechanically triggered covalent reactions in the solid state include the stress induced ring opening of spiropyran to a colored merocyanine, the cycloreversion of cyclobutane, and mechanically responsive materials based on Diels–Alder/retro-Diels–Alder reactions. A common difficulty in quantifying a mechanical response in polymeric materials is the inherently low numbers of mechanochemical events taking place under stress. Bulk polymeric materials under stress often have highly localized, overstressed bonds at which the mechanochemical transformations occur.

The inherently low levels of mechanochemical events have required analytically sensitive techniques such as fluorescence and absorbance spectroscopies to detect activation, and they in general provide qualitative and/or low resolution (microscopic as opposed to molecular) descriptions of force distributions in polymeric materials. Important questions remain as to (a) how many monomers along a polymer experience what magnitudes of force, and for how long; (b) the distribution of stressed monomers along polymer chains; and (c) how ‘a’ and ‘b’ vary for different macroscopic loading environments.

In order to probe these questions, it is desirable to employ materials that have high densities of mechanically active linkages, the mechanochemical activation of which is both irreversible and results in reaction products that can be quantified spectroscopically. The interrogation of such materials might provide not only evidence of the presence of mechanical activation, but more importantly information regarding the localized (i.e., within individual polymer molecules) mechanical environment. In this regard, one promising platform is achieved by the addition of dihalocarbene to polybutadiene, resulting in *gem*-dihalocyclopropanes (gDHCs) along the polymer main chain. The gDHCs are proven mechanophores, and when embedded in a polymer backbone, their electrocyclic ring opening to the corresponding 2,3-dihaloalkenes (Fig. 1) is well coupled to mechanical force. Literally hundreds of incorporated *gem*-dichlorocyclopropane rings along a single polymer chain have previously been shown to react in response to tensile forces
generated by sonication or force microscopy. The products of the rearrangement are easily observed with $^1$H NMR, which, in addition to being straightforward and quantitative, offers the advantage that the chemical shifts of the resonances are sensitive to the localized, chemical environment in a way that permits characterization of the chemical microstructure of the polymer.

Herein we report that polymer-embedded gDHCs are activated in the solid state as a function of compressive stress. Analysis of the $^1$H NMR spectra provides information regarding the size of the mechanically activated domains, here judged in terms of the block length of activated monomers ($X$ in Fig. 1). In contrast to the activation observed under compression, tensile loads on the same bulk polymers do not result in detectable levels of mechanophore activation, even when the materials are loaded to the point of failure.

2 Experimental

Synthesis

1,4-cis-polybutadiene, cetyltrimethylammonium bromide (CTAB), sodium hydroxide (NaOH), bromoform and dichloromethane were purchased from Sigma Aldrich, and chloroform (CHCl3), methanol (CH3OH) and dichloromethane (CH2Cl2) were purchased from VWR. Difluorinated versions of mechanophore activation very difficult. The new products, making quantification of small amounts of activation very difficult. The gDHC–PB polymers were synthesized by adapting previously reported methods, as described here for the gDCC-functionalized PB.

To a stirring solution of 0.19 M 1,4-cis-polybutadiene and 11 mol percent of CTAB in CHCl3 under N2 was added dropwise 7 equivalents of NaOH in 50 mL of deoxygenated DI H2O. The reaction was stirred at room temperature for 18 hours under a headspace of N2. Workup consisted of washing the polymer 3 times with ca. 200 mL 1:1 brine: DI H2O and then concentrating the organic layer to minimal volume and precipitating with CH2OH. The precipitated polymer was then redissolved in CH2Cl2, concentrated, and reprecipitated with CH2OH. The polymer was dried extensively on a high vacuum line prior to experiments. The percent functionalization was determined to be >98% based upon integration of relevant resonances in $^1$H NMR (see ESI† for details). To verify that the ring opening is mechanically induced, rather than an indirect pressure-induced effect, similar compressions were performed on identical samples, but the pressure was held for varying lengths of time from 15 to 600 seconds. As shown in Fig. 2a, the extent of ring opening was independent of the time over which the pressure was maintained (0.10 ± 0.01%), indicating that the activation occurs during the initial pressure-induced deformation of the polymer rather than while the deformed polymer is held under a static pressure. Greater pressure leads to larger macroscopic deformation, local strains, and therefore higher forces on individual polymers. The extent of ring opening scaled nearly linearly with applied pressure over a range of 36 to 249 MPa. Finally, we note that these polymers, stresses, and strain rates. First, the polymer was compressed to a final pressure of 178 MPa, at which it was held for 6.25 minutes. Subsequent $^1$H NMR analysis revealed that ca. 0.09% of the gDCC mechanophores ring opened to the corresponding 2,3-dichloroalkenes during the compression (peak intensities normalized to unreacted polybutadiene peaks; see ESI† for details). To verify that the ring opening is mechanically induced, rather than an indirect pressure-induced effect, similar compressions were performed on identical samples, but the pressure was held for varying lengths of time from 15 to 600 seconds. As shown in Fig. 2a, the extent of ring opening was independent of the time over which the pressure was maintained (0.10 ± 0.01%), indicating that the activation occurs during the initial pressure-induced deformation of the polymer rather than while the deformed polymer is held under a static pressure. Greater pressure leads to larger macroscopic deformation, local strains, and therefore higher forces on individual polymers. The extent of ring opening scaled nearly linearly with applied pressure over a range of 36 to 249 MPa. Finally, we note that these
experiments set an upper limit of several seconds for the time scale of the mechanically activated gDCC ring opening under these conditions.

Applying pressure to an already compressed sample resulted in no additional activation, consistent with a force-induced mechanism rather than a pressure-induced mechanism. We next investigated the effects of altering the polymer geometry during compressive testing. Flipping the compressed polymer sample in between repeated presses (178 MPa), for example, had no measurable effect; the extent of ring opening over a series of five different presses remained consistent with the single-press value of 0.09 ± 0.04%, independently of the number of times the sample was removed and flipped over in between presses. The amount of ring opening did, however, increase if the polymer was instead folded in half between presses, so that it was thicker and able to be deformed by the compression. Over one series of 12 fold/compression cycles, for example, the amount of ring opening varied linearly with the number of cycles, ultimately reaching a final mechanophore conversion of 2.8%.

That thermal contributions to the process are negligible was supported by monitoring the rearrangement products of gem-dibromo (gDCC: 87% cis-gDCC, 13% PB) and gem-bromo-chlorocyclopropanated (gBCC: 80% gBCC, 20% PB) polymers. Both gDCC and gBCCs ring open in a disrotatory fashion through allyl cation-like transition states to form 2,3-dihalocyclopropanes.\(^{17}\) We first analyzed the thermolytic reactions of these polymers. Consistent with previous reports, heating the gDCC polymer for 17 hours (165 °C, methyl benzoate, \(N_2\)) led to the formation of both 2,3-dibromoalkene and subsequent HBr elimination products,\(^{18}\) as observed by \(^1\)H NMR (see Fig. S23†). Identical thermolysis of the gBCC polymer led to the selective formation of a single isomer: the cis-anti-Br as opposed to the cis-syn-Br (solvolytic rearrangements of gBCC isomers have previously established a thermal selectivity of ~970 : 1 in favor of the cis-anti-Br isomer\(^{19}\)). In addition, we observed the formation of products from the subsequent elimination of HBr from the 2,3-chlorobromoalkene.

These reaction outcomes differ when the reaction is induced mechanically, rather than thermally. Pulsed ultrasound of polymer solutions, for example, is an efficient way to apply large mechanical forces along the polymer backbone and sonication of the gDBC polymer led to exclusive formation of 2,3-dibromoalkene with no subsequent HBr elimination. Similarly, sonication of the gBCC polymer led to nearly equivalent ring opening of the cis-anti-bromochloro and cis-syn-bromo-chlorocyclopropane isomers (see ESI†).

The outcomes induced by compressive force are also different from the thermal reactions and similar to those from the sonochemistry. First, we observed \(^1\)H NMR no evidence for HBr elimination products due to compression of either the gDBC or gBCC polymer (see ESI†). Second, whereas thermolysis of the gDBC polymer result in the selective ring opening of the cis-anti-bromochloro isomer, both isomers were observed to ring open during compressive activation (Fig. 3). Product analysis by \(^1\)H NMR led to a reactivity ratio of 1.8 : 1 for cis-anti-Br versus cis-syn-Br during compressive stress—to our knowledge the first example of determining the reactivity ratio of competing reactions in the solid state. The lack of isomeric selectivity during both sonochemical and compressive activation of gBCC polymer is consistent with previously described, nearly unselective mechanochemical competition experiments,\(^{13,20}\) and support a dominant mechanical contribution to gDHC ring opening by compressive stress.

Next, the solid state ring opening of gDHC polymers allowed us to compare the effects of changing the loading environment from compressive to tensile deformation (Fig. 4). A solution cast, vacuum dried polymer film was first subjected to direct monotonic tension at 25 °C. Upon polymer failure, the gauge section of the failed sample was dissolved in CDCl\(_3\) for \(^1\)H NMR analysis. No evidence of the gDCC ring opening was observed in the \(^1\)H NMR spectrum (Fig. 5). Recent work by Lee et al.,\(^{21}\) demonstrated that “prestretching” to align polymer chains in the direction of force promotes mecanochemical activation. Following from Lee et al., the samples were prestretched and held for 600 seconds at a stretch ratio of 8 (see ESI†). These plastically deformed samples were then retested in tension, resulting in a higher stress at failure. \(^1\)H NMR analysis again indicated that the gDBC polymer was mechanically silent. Tensile experiments were then conducted on dynamic mechanical analysis equipment to control the temperature of the polymer. Samples were tested at a range of temperatures near and below \(T_g (\sim 10 °C)\) in order to impart higher force to the polymer and across the mechanophore. While substantially higher stresses were applied, again no activation was apparent in the \(^1\)H NMR spectra.
Solid-state reactivity in the gDHCs follows what is initially a counterintuitive trend; macro-scale tensile forces prove ineffective where compression leads to significant ring opening. We note first that whereas the macroscopic forces that lead to activation are compressive, the individual mechanophores likely experience both tensile and shear forces which cause ring opening. The exact distribution of stresses and strains experienced at the molecular level in these experiments is beyond the scope of this study, but the results motivate further experimental and theoretical work on that topic. In addition, while the experiments presented earlier in this manuscript show that the activation is strain (and presumably strain-rate) dependent, rather than purely stress-dependent, it is interesting to consider the magnitude of the stresses in the two experiments. For example, room temperature tensile testing of gDBC leads to maximum stresses of ca. 0.2 MPa while the smallest stresses applied during compression is 36 MPa. At the lowest compressive stresses, the percent of mechanophore activity is vanishingly small at ca. 0.1% (gDCC) and ca. 0.4% (gDBC). From the linear regression analysis obtained from gDBC ring opening activation during compression, an achieved tensile stress of 0.2 MPa would lead to ca. 2 × 10⁻³% ring opening, a value likely below the sensitivity of the NMR measurement. The largest stress associated with the tensile testing is ca. 14 MPa (monotonic tensile testing to failure, −25 °C) and an expected ring opening percent of 0.11 is near the limit of NMR detection. For comparison, mechanical activation of spiropyran in polymers under macroscopic tension has been observed at stresses of approximately 30–50 MPa, with a very recent report showing some activation at stresses slightly below 20 MPa.

Of particular interest to us was the opportunity to use the ¹H NMR spectra to characterize the microstructure of the
mechanically activated domains, in particular the block length (N in Fig. 1) of the activated segments. For example, we wondered to what extent the activation of adjacent monomers is correlated. The extent of ring opening per compression varies from 2 to 7 activated mechanophores per polymer chain, depending on the polymer molecular weight, mechanophore, and conditions. At one extreme, one can imagine that this mechanochanical response is dominated by a few, long chain segments (in only a small fraction of the polymer chains) in which all mechanophores are activated, leading to large blocks of 2,3-dihaloalkenes. At the other extreme, mechanical stresses could be concentrated on isolated monomers, leading to isolated 2,3-dihaloalkenes. Our interest in this question is driven by both practical (e.g., the ability to trigger localized cross-linking) and fundamental (e.g., the nature of molecular stress distributions in macroscopic materials) concerns.

The mechanochemically active domains can be characterized by \textsuperscript{1}H NMR, because the chemical shifts of the resonances are indicative of polymer microstructure. For example, sonochemical activation of gDCC polymer led to \textsuperscript{1}H NMR signals at 5.85 ppm (vinyl) and 4.46 ppm (allylic), whereas thermolysis generated product resonances at 5.95 ppm (vinyl) and 4.52 ppm (allylic). The differences in chemical shift are not due to alkene stereochemistry, as 1D NOESY spectra show coupling between the vinylic and allylic peaks in both products, indicating that each alkene was the (Z) product. The product \textsuperscript{1}H NMR resonances are instead indicative of ‘bloppy’ versus ‘random’ repeating segments along the polymer chain. For example, rearrangements imposed by pulsed ultrasound are induced by the accumulation of force at the polymer midchain,\textsuperscript{22} where large numbers of mecanochemical events, including polymer scission, occur.\textsuperscript{18} This concentration of force leads to highly blocky products from pulsed ultrasound,\textsuperscript{23} corresponding to the alkene resonance at 5.85 ppm.

In contrast, thermal activation is a random process in which the probability of \textsuperscript{1}H NMR chemical shifts from sonochemically activated gDCC polymer indicate the presence of distinct microstructural environments along the polymer. Compressive gDCC activation leads to \textsuperscript{1}H NMR product resonances consistent with a mixture of the two chemical environments. Thermal and sonochemical data taken from ref. 23.

Fig. 5 \textsuperscript{1}H NMR chemical shifts from sonochemically activated gDCC polymer lead to \textsuperscript{1}H NMR product resonances comprising both sets of resonances. The \textsuperscript{1}H NMR spectra from compressively activated gDCC polymers were deconvoluted using a Lorentzian curve fitting function with Origin\textsuperscript{9} software to determine the relative areas at each peak position. From analysis of 8 compressively activated samples, an average integrated area of 3 ± 0.2 : 1 was determined for peak areas at 5.85 ppm (‘adjacent’) : 5.95 ppm (‘isolated’). The ‘isolated’ resonance at 5.95 represents a terminal monomer of a mechanically activated domain, but not all terminal monomers contribute to this peak because of the relative orientation of the 2,3-dichloroalkene. If a terminal 2,3-dichloroalkene in the activated block is oriented ‘allyl out’, then it contributes to the intensity at 5.95 ppm. On the other hand, if a terminal 2,3-dichloroalkene is oriented ‘allyl in’, the resonance shows up at 5.85 ppm. Assuming that the directionality of the ring opening is random, this means that there are on average 2 internal and 2 terminal 2,3-dichloroalkenes per mechanically activated domain, or a block length of roughly 4 monomers.

The size of the mechanically active domains is clearly larger, therefore, than a single monomer, in that the activation of adjacent monomers is much more frequent than would result from random statistics. The size of the domains is much smaller, however, than typical average entanglement spacings, which are on the order of tens of monomers.\textsuperscript{24} A molecular interpretation of these observations is not obvious, because conventional models of polymer mechanics do not account for different forces along a stress-bearing chain segment between entanglement points. We propose three possible effects that might contribute, alone or in combination, to the observed domain sizes.

First, entanglement spacings are certainly not monodisperse, and it is possible that the shortest stress-bearing chain segments are the most likely to become overstressed and mechanically
activated. Thus, the observed activated domain sizes might reflect the presence of a relatively large number of very small entanglement spacings. Four monomers is, to us, an unexpectedly small entanglement spacing to be present in these quantities, but we acknowledge that our objection is more intuitive than quantitative. A second possibility is that the relevant stressed domains are on the order of tens of monomers but that the local mechanophane rearrangement provides localized “stress relief” through an irreversible extension of contour length, as characterized previously using single molecule force spectroscopy. In this picture, the activation of one monomer serves to provide “slack” along the stress-bearing chain, reducing the load on other monomers and preventing the complete remodeling of the overstressed chain segment. For such a picture to be consistent with the experimental observations of activated clusters of monomers, the force would necessarily be concentrated within the active chain segments, as observed for example in the extensional shear flows that accompany sonication of polymer solutions. Finally, we consider the possibility that the forces are localized not by the dynamics of shear flow but by topological contributions. For example, the forces right at the entanglement points themselves might be different than the forces between entanglements, or the activity might reflect the presence of knots and the concentration of forces at their entrances and exits. Any mechanism must account for the additional fact that the size of the domains is fairly insensitive to the applied stress/strain and the extent of activation: compression of one series of gDCC–PB at 107, 142, 160, 178, and 249 MPa gives extents of ring opening that increase linearly from 0.56% to 0.97%, but the ratio of internal to terminal allylic protons remains constant within experimental uncertainty (2.4, 3.6, 3.0, 3.3, and 2.9, respectively). We acknowledge that our suggestions as to the underlying physics are speculative only, but we hope that the core, unanticipated observation of localized mechanically active domains of several monomers should serve to motivate further experimental and theoretical investigations of mechanically active domain sizes in polymeric materials.

Finally, we note that these results have implications for the design of stress-responsive and/or self-healing materials through mechanoochemical activation. The regions of highest stress, even within an individual polymer, are shown here to be highly localized—on the order of a handful of monomers. If the incorporation of stress-responsive mechanophanes is to be used to signal, prevent, and/or repair the damage brought about by molecular stresses, then, at least in some cases, it is likely to be important to have high densities of mechanophanes in the at-risk regions. In the case presented here, mechanophane densities of less than 1 out of 4 monomers would lead to some instances of no response from regions of very high (>nN) molecular stress.

4 Conclusions

Compressive force, when applied to highly functionalized gem-dihaloacylcopropane polymers, can be used to effect the localized, electrocyclic ring opening of gDHC mechanophanes. The average block length of mechanically activated monomers along a polymer backbone was determined to be ca. 4 monomers. Mechanical activation of adjacent monomers is therefore correlated, but not completely so over lengths that are typical of that between entanglements. In contrast to the activity observed in compression, tensile load resulted in no measurable activation, even when applied to the point of failure. To the best of our knowledge, these are the first characterizations of mechanically activated domains within a macroscopic material from a molecular, rather than continuum, frame of reference. Although the details are likely to be specific to the polymers tested and the conditions employed, these results support a picture in which the critical domain for mechanical activation in polymers is greater than a single monomer and must account for heterogeneous response over distances smaller than the average entanglement spacing.

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References