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Microstructure of Copolymers Formed by the Reagentless, Mechanochemical Remodeling of Homopolymers via Pulsed Ultrasound

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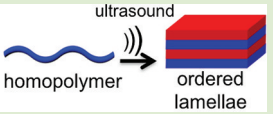
Supporting Information

ABSTRACT: The high shear forces generated during the pulsed ultrasound of dilute polymer solutions lead to large tensile forces that are focused near the center of the polymer chain, but quantitative experimental evidence regarding the force distribution is rare. Here, pulsed ultrasound of quantitatively *geminal*-dihalocyclopropanated (*g*DHC) polybutadiene provides insights into the distribution. Pulsed ultrasound leads to the mechanochemical ring-opening of the *g*DHC mechanophore to a 2,3-dihaloalkene. The alkene product is then degraded through ozonolysis to leave behind only those stretches of the polymer that have not experienced large enough forces to be activated. Microstructural and molecular weight analysis reveals that the activated and unactivated regions of the polymer are continuous, indicating a smooth and monotonic force distribution from the midchain peak toward the polymer ends. When coupled to chain scission, the net process constitutes the rapid, specific, and reagentless conversion of a single homopolymer into block copolymers. Despite their compositional polydispersity, the sonicated polymers assemble into ordered lamellar phases that are characterized by small-angle X-ray scattering.



The use of pulsed ultrasound as a method for triggering mechanochemistry along a polymer main chain has gained great popularity over the past decade. A long history of ultrasound-induced polymer chain scission has now been complemented by mechanochemical electrocyclic ring openings,[1−4] the activation of latent catalysts,[5−7] the isomerization of atropisomers,[8] the reversal of cycloaddition reactions,[9] and the trapping of diradical transition states.[10] The technique has found utility as a screening tool for mechanical activity because of the large forces (>nN), convenient sample quantities (mg), and ease of analysis associated with these reactions, which are typically conducted in dilute or semidilute solutions. Several aspects of the mechanochemical process are well appreciated, and both theoretical and experimental evidence point to a preference for midchain activity, of either the scissile or nonscissile variety, during pulsed ultrasound.[11−13] The forces are the greatest at the center of the polymer chain, and while quantitative experiments have yet to be reported, it is believed that the force drops monotonically from its peak near the center to the chain ends. Here, we use a combination of scissile and nonscissile mechanochemistry to probe the smoothness of the force distribution. In particular, we find that a solution of a single homopolymer can be mechanochemically remodeled (almost literally "in a snap") into well-ordered, albeit somewhat polydisperse, block copolymers, providing experimental support for a highly smooth and monotonic force distribution in these processes. Beyond the insights into force distributions, potential utility of the approach is suggested by the demonstration that sonication of a homopolymer leads to a product that assembles into ordered lamellae.

The hypothesis driving our idea is described in Figure 1. When subjected to the extensional shear forces associated with cavitation bubble collapse in pulsed ultrasound, the polymer chain begins to stretch and forces build up along the backbone, activating the mechanophores near the center of the chain where the forces are concentrated. For peak forces of sufficient magnitude, the value of the midchain force increases along with the zone of activation until the covalent bonds of the polymer can no longer withstand the force and the polymer breaks near the middle of the activated region. The chain scission event leaves behind two segments, each being close to half of the molecular weight of the original polymer and possessing a similar content of activated mechanophore, determined by the magnitude of the forces and the activity of the mechanophore. The question we set out to answer is whether or not the distribution of forces is such that the activated region (red in Figure 1) is continuous or whether there is an extended region over which a mixture of activated and nonactivated mechanophores are found. There are clearly large forces at which mechanophore activation is certain to occur and forces below which mechanophore activation is certain not to occur, but there must also be a range of forces over which mechanophore activation may or may not occur on the time

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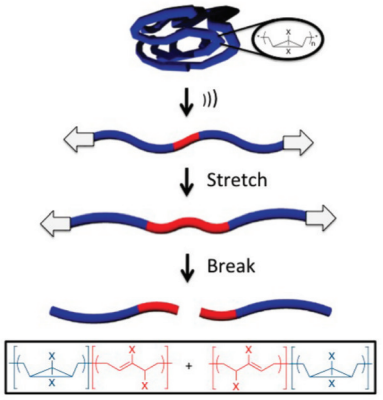


Figure 1. Pulsed ultrasound of *gem*-dihalocyclopropanated polymer leads to the ring-opening reaction of *g*DHCs to 2,3-dihalolalkenes (X = Cl, X = Br) at rates dependent on the proximity of the mechanophore to the center of the polymer chain. The combination of targeted activation and chain scission leads to the formation of well-defined block copolymers.

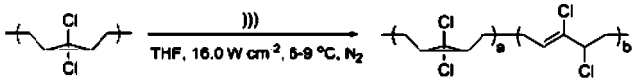
scale of the event (the blue-to-red interface in Figure 1). Is the size of this "maybe" region large or small relative to the active/inactive zones? If the answer is that the region is small, then is there sufficient structural information in the products to create ordered microphases simply through a combination of ultrasound and a solution of homopolymers?

A test of the proposed scheme requires homopolymers that are densely populated with mechanophores, which can be be efficiently activated under sonochemical shear. We recently reported that *gem*-dichlorocyclopropanes (*g*DCCs), generated along the main chain of polybutadiene (94% 1,4), fulfill these criteria,[2] although the key question of product microstructure have not been addressed previously by us or by others. Extensive reaction of polybutadiene with dichlorocarbene yielded a polymer of close to 100% *g*DCC content with number-averaged molecular weight (M_n) of 370 kDa. Subsequent ozonolysis cleaved the few unfunctionalized double bonds, giving a 93 kDa polymer that is 100% *g*DCC by ^{1}H NMR.

This *g*DCC polymer was then subjected to pulsed ultrasound (16.0 W cm^{-2}, 3.1 mg mL^{-1} in THF, 6−9 °C, pulsed 1 s on/1 s off) until the average molecular weight was either just above (30 min, 51 kDa) or just below (60 min, 43 kDa; 120 min, 41 kDa) half its initial value. At three time points, ^{1}H NMR analysis showed that 49% (30 min), 54% (60 min), and 58% (120 min) of the *g*DCCs had opened to the expected 2,3-dichloroalkene products (Table 1). Diagnostic ^{1}H NMR resonances were then used to characterize the chemical microstructure: sonochemical activation of *g*DCC polymer gives product ^{1}H NMR signals at δ 5.85 ppm (vinyl) and 4.46 ppm (allylic), in comparison to thermolysis generated product resonances at δ 5.95 (vinyl) and 4.52 ppm (allylic).[3] Shown in Figure 2 is an overlay of an 89 kDa, 100% *g*DCC polymer, representative of those used in this study, that was thermolyzed as well as sonicated to one scission cycle. The differences in chemical shift between the samples are substantial and well beyond the measurement uncertainty (<0.01 ppm).

The differences in chemical shift do not derive from alkene stereochemistry, as 1D NOESY spectra reported previously show coupling between the vinylic and allylic peaks in both products, indicative of exclusive (*Z*)-alkene formation.[3] The differences in the product ^{1}H NMR resonances are instead

Table 1. Sonication and Subsequent Ozonolysis of 93 kDa 100% poly(*g*DCC) Polymer[a]



sonication time (min)	M_n (kDa)	PDI	a	b	M_n^{calc} (kDa)	M_n^{obs} (kDa)
30	51	1.1	0.51	0.49	30	32
60	43	1.1	0.46	0.54	21	21
120	41	1.1	0.42	0.58	20	20

[a] M_n^{calc} is the expected average M_n of the "a" segment, assuming perfect diblock structure; M_n^{obs} is the measured M_n (MALS-GPC) of the "a" block following ozonolysis of the "b" block.

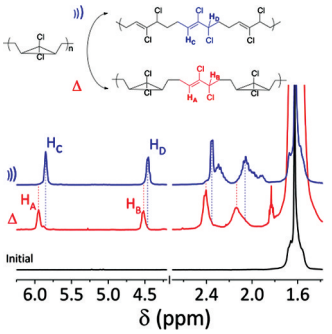


Figure 2. Thermal [red △; 180 °C, methyl benzoate, N_2, 4 h] vs sonochemical [blue))); 6−9 °C, THF, N_2, 70 min, 12.4 W cm^{-2}] activation of a 89 kDa 100% *cis*-*g*DCC polymer. Chemical shifts of the formed 2,3-dichloroalkenes provide insights into the local chemical environment of the ring-opened *g*DCC.

ascribed to "blocky" versus "random" repeating segments along the polymer chain. (Figure 2) Thermal activation is a random process, in which the probability of *g*DCC ring-opening is effectively independent of position along the polymer. At low thermal conversions of *g*DCC, the vinyl proton resonance at δ 5.95 ppm corresponds to that from a 2,3-dichloroalkene that is adjacent to an unopened dichlorocyclopropane. This assignment is further supported by chemical shifts of the methylene protons that are adjacent to the 2,3-dichloroalkene product. Thermal activation of *g*DCC polymer leads to methylene resonances at δ 2.41 and 2.15 ppm, whereas the products from sonochemical treatment led to methylene resonances at δ 2.36, 2.30, and 2.06 ppm, of which the 2.36 and 2.30 ppm resonances together integrate 1:1 relative to the peak at 2.06 ppm and are ascribed to head-to-head versus head-to-tail orientation of adjacent 2,3-dichloroalkenes. We assume (but do not attempt to characterize) that the activated blocks are aregic. The adjacent methylene peaks therefore also report on the adjacent (δ 2.36−2.30 ppm) versus isolated (δ 2.41 ppm) position of the mechanically activated monomers. While we cannot conclude that the diblock structure is "perfect", the number of "imperfections" is too small to be detected by ^{1}H NMR (<5%). This conclusion supports the model described in Figure 1 of focused regions of activity emanating from the center of the polymer chain.

Further, complementary support for blocky character comes from ozonolysis of the sonicated polymer, leading to the selective degradation of the olefinic products of the mechanochemical reaction (Figure 3). For example, sonication of a 93 kDa *g*DCC polymer furnished a mixture of polymers with an average molecular weight of 51 kDa and monomer

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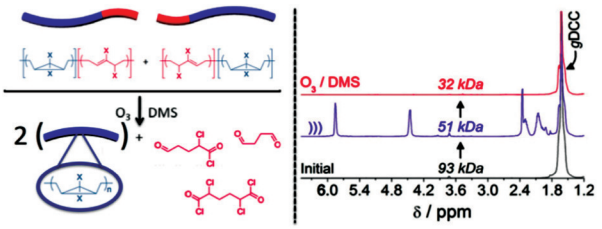

Figure 3. Support for the formation of diblock copolymers is obtained by subjecting the polymer to ozonolysis (workup with dimethylsulfide; DMS). Ozonolysis cleaves the formed 2,3-dichloroalkenes to oxidized products, leaving an intact poly(*g*DCC), the molecular weight of which is equivalent to that expected for a pure block.

content that is 49% 2,3-dichloroalkene and 51% *g*DCC. To facilitate a quantitative analysis we assume that all of the initial parent polymers are activated/broken once before the daughter polymers are activated/broken a second time. This assumption is certainly not true, but it is likely to be a reasonable assumption for these purposes because the final M_n after one scission (46.5 kDa) is close to the limiting molecular weight for sonochemical activation, and so "second generation" activation/scission events should be a minor component of the observed activity. Assuming a blocky structure, the *g*DCC block per polymer is calculated to have $M_{n,gDCC}$ = 30 ± 3 kDa (see Supporting Information, SI). Ozonolysis was used to cleave the 2,3-dichloroalkenes, and subsequent methanol precipitation separated the untouched *g*DCC blocks from the low molecular weight ozonolyzed products; the precipitated polymer is "pure" poly(*g*DCC) by ^{1}H NMR (no vinyl proton resonances, see Figure 3). The average molecular weight of the precipitated polymer was measured to be 32 ± 3 kDa, within experimental uncertainty of the total *g*DCC content (30 kDa), indicating that the *g*DCCs are continuous within a single block. The mass recovery of poly(*g*DCC) from the ozonolysis experiments was 96% of the theoretical value, and so the analysis is representative of the true *g*DCC block sizes after sonication. Similar analyses were conducted on 93 kDa *g*DCC polymer sonicated to 43 and 41 kDa with ring-opening percentages of 54 and 58%, respectively. Subsequent ozonolysis of these sonicated polymers and methanol precipitation led to recovery of polymers that are pure *g*DCC by ^{1}H NMR and with number-averaged molecular weights of 21 kDa (theoretical M_n = 21 kDa) and 20 kDa (theoretical M_n = 20 kDa). We reiterate that these comparative analyses are based on assumptions that do not capture the full distribution of responses, but it is clear that sonochemical activation provides polymers with large blocks of activated and inactivated domains.

Interest in diblock copolymers stems from their ability to organize into discrete objects in solution (e.g., vesicles) and ordered, microphase-separated morphologies in the solid state. Thus, we wondered if the mechanically remodeled blocks were of sufficient size and purity to exhibit properties that are distinct from those of the unactivated blocks. In that regard, we were encouraged to find that differential scanning calorimetry (DSC) of 134 kDa poly(*g*DCC), sonicated for 22 min to give a final molecular weight of 67 kDa, exhibited two glass transition temperatures, suggestive of separation of the block copolymer into distinct homopolymer-rich domains.[14−17] Although the observed T_gs of microphase separated blocks typically differ from those of the corresponding homopolymers,[14] we attribute the midpoints of the two endotherms, at 2 and 21 °C, to the poly(*g*DCC) (T_g of ∼0 °C) and activated alkene blocks, respectively (see SI). We note that the observation of two T_gs does not necessarily imply a well-ordered microphase separation (or even any microphase separation).[18] The diblocks generated here are certainly more polydisperse than those generated by controlled/"living" polymerization techniques,[19,20] because high molecular weight polymers are more prone to mechanical activation than are low molecular weight polymers.[21,22] The increased activity of higher molecular weight polymers leads to a well-known narrowing of the molecular weight distribution during sonication,[21] but in the context of the remodeling work reported here, it means that some of the ultimate polymer solution must contain polymer strands that have undergone more than one scission cycle, while others have yet to be activated, and some have been activated but not cleaved. Whereas the overall molecular weight distributions are reasonably narrow (Table 1), the stochasticity of the obtained chain microstructures results in variations in the volume fraction of unopened *g*DCC blocks from chain to chain.

Recent reports have demonstrated that chain length and composition polydispersity do not preclude microphase separation[23−26] and that polydispersity can actually stabilize microphase-separated polymer morphologies.[27] Synchrotron small-angle X-ray scattering (SAXS) patterns of annealed samples of the 67 kDa copolymers revealed the formation of an ordered lamellar morphology (d = 27 nm), confirming microphase-separation in our block copolymers (Figure 4). The

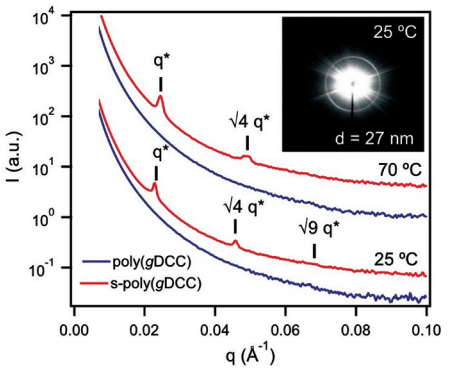

Figure 4. Azimuthally integrated intensity, v, scattering wavevector, q, plots of synchrotron small-angle X-ray scattering patterns obtained from an annealed (70 °C) 134 kDa poly(*g*DCC) polymer (blue) before and after sonication to a final weight of 67 kDa (red). These data indicate formation of a lamellar morphology with d = 27 nm at 25 °C that persists in the melt phase at 70 °C, indicative of a chemical incompatibility-induced microphase separation.

persistence of this morphology above the melting temperature of the poly(*g*DCC) blocks (T_m = 42 °C in the copolymer) implies that chemical incompatibility between the dissimilar blocks drives this melt microphase separation. The observed domain spacing of 27 nm is typical for polystyrene−polyisoprene copolymers of comparable molecular weights.[28]

In conclusion, the combination of microstructural analysis by ^{1}H NMR and chemical degradation analysis by ozonolysis strongly support highly continuous, "blocky" character in the reagentless sonochemical conversion of poly(*g*DCC) to the 2,3-dichloroalkenylated product. The polymer microstructure provides experimental evidence of a monotonic force gradient along the polymer chain during pulsed sonication, which transitions rapidly from mechanically active to inactive zones in the context of the ring-opening reaction. While these blocky

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copolymers exhibit both chain length and composition polydispersities, DSC and SAXS results demonstrate that in some situations the application of ultrasound alone (followed by isolation and annealing), in the absence of any additional reagents, can be used to create not only molecular order, but ordered supramolecular morphologies. The specific *g*DCC systems might therefore find practical utility, yet we believe that the general approach proven here has several potential advantages that extend beyond this proof-of-concept demonstration. First, it has been demonstrated that new reactions and exotic species can be generated by the mechanical forces involved in polymer sonochemistry,[5,8] including structures such as diradical transition states that cannot be harnessed under any other reaction conditions.[10] The mechanochemical route might therefore provide access to otherwise unattainable polymer functionalities. Second, reactions that typically require high temperatures and/or harsh conditions can be activated mechanically, while the remainder of the polymer (groups that are not both in the center and coupled to the tension in the main chain) experiences a mild environment (here, <10 °C in THF). Third, the unactivated groups (e.g., the unopened *g*DCC blocks here) could be subsequently activated thermally,[29,30] providing access to further decorated diblock copolymers. These attributes differ substantially from those provided by the conventional shear-induced diblock copolymer syntheses, wherein free radicals generated at the chain ends by polymer chain scission initiate either controlled[31] or uncontrolled[32] free radical polymerizations, an approach that is conceptually more similar to linear diblock syntheses and graft polymerizations. Lastly, we note that the mechanochemical remodeling reported here is reasonably regarded as an example of fairly extreme regioselective synthesis, a fact that holds some aesthetic appeal that complements its utility.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Information includes the synthesis and characterization of polymers, sonicated products, and ozonolysis products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

*g*DCC, *geminal*-dichlorocyclopropane; M_n, number averaged molecular weight; GPC, gel permeation chromatography; NMR, nuclear magnetic resonance; DMS, dimethylsulfide; *g*DBC, *geminal*-dibromocyclopropane; DSC, differential scanning calorimetry; SAXS, small-angle X-ray scattering

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