Mechanically Induced Scission and Subsequent Thermal Remending of Perfluorocyclobutane Polymers

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ⓢ Supporting Information

ABSTRACT: Perfluorocyclobutane (PFCB) polymer solutions were subjected to pulsed ultrasound, leading to mechanically induced chain scission and molecular weight degradation. ^{19}F NMR revealed that the new, mechanically generated end groups are trifluorovinyl ethers formed by cycloreversion of the PFCB groups, a process that differs from thermal degradation pathways. One consequence of the mechanochemical process is that the trifluorovinyl ether end groups can be remended simply by subjecting the polymer solution to the original polymerization conditions, that is, heating to >150 °C. Stereochemical changes in the PFCBs, in combination with radical trapping experiments, indicate that PFCB scission proceeds via a stepwise mechanism with a 1,4-diradical intermediate, offering a potential mechanism for localized functionalization and cross-linking in regions of high stress.
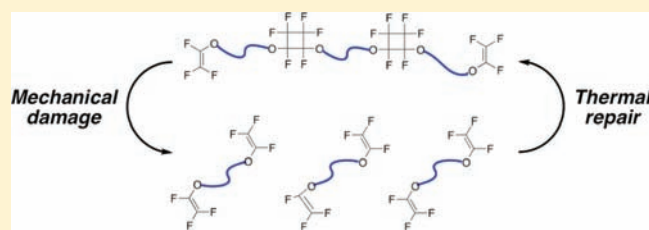
■ INTRODUCTION

Polymeric materials that are either self-repairing or easily remendable are of considerable current interest, because the ability to reverse mechanical damage suffered under load might prevent catastrophic failure and extend the useful lifetime of engineering and/or biomedical materials in situations where replacement is difficult and/or expensive.[1−4] Ideally, thermal remending must reverse the molecular scale, mechanical destruction of topological (e.g., entanglements),[5] physical (e.g., supramolecular),[6−8] or covalent[9] interactions. When considering mechanically induced covalent damage, recent studies have demonstrated not only how mechanical forces lead to the rupture of covalent[10] and coordinative[11−14] bonds, but also that new bonds can form either during or immediately following a period of high stress.[15−17] Here, we report that perfluorocyclobutane aryl ether polymers possess both of these desirable mechanical responses, mechanically triggered formation of new bonds during stress and thermal remending following scission, in a single mechanophore.

The concept of thermal remending of covalent bonds was first reported by Wudl and co-workers, who devised a polymeric material that would fail through a thermally reversible retro−Diels−Alder reaction when subjected to load in the solid state,[9] and Bielawski has recently demonstrated that the same process can be triggered by shear in solution.[18] Both bond breaking processes can be reversed by heat.[9,18] Sijbesma demonstrated further that by engineering reversible coordination bonds into a polymer, the molecular weight can be degraded and restored indefinitely.[14] Broadly, the challenge for the covalent remending strategy is to find bonds that are (1) stable and strong enough to fulfill the structural properties of interest; (2) fail under high load

to give products that can repolymerize when desired; and (3) can be introduced at high density within the material, so that they, rather than undesired alternatives, are the site of mechanical failure (Figure 1).

In addition to controlling the mechanism of bond scission to facilitate remending, a complementary strategy for property enhancement might be to mechanically trigger new bond forming reactions along an otherwise intact polymer backbone.[19] For example, Moore showed that when poly(ethyleneglycol) (PEG) tethered benzocyclobutane (BCB) groups were stressed in the presence of a maleimide chromophore, the stress-induced ring-opening of the BCB to an *ortho*-quinodimethine resulted in cyclo-addition to the maleimide dienophile without chain scission.[16] It has also been demonstrated that substitution reactions can occur following mechanochemical activation, through the nucleophilic substitution of an allylic bromide product formed from the mechanically triggered ring-opening of *gem*-dibromocyclopropane (*g*DBCs).[15] Mechanically generated radicals are potentially interesting for stress-induced chemistry, and *gem*-difluorocyclopropane (*g*DFC) mechanophores have been shown to undergo force-induced ring-opening to create multiple diradicals along a stressed polymer chain.[17,20] These diradicals can be trapped by intermolecular radical addition reactions, creating a pathway for stress-responsive reactivity. These previous examples represent an expanding range of potential strategies for localized, "on-demand" stress-induced cross-linking in the solid state, although

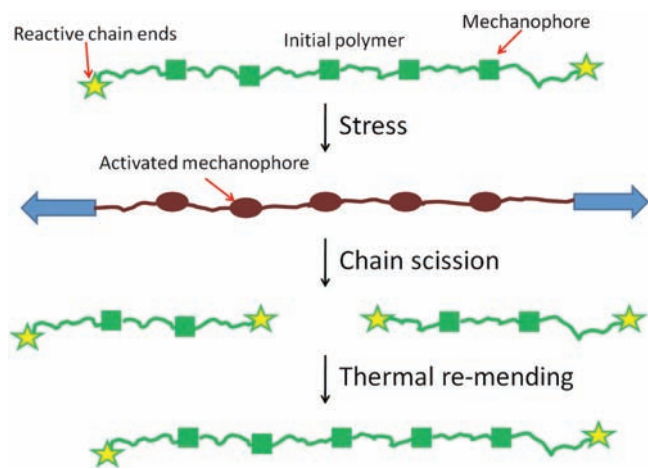**Figure 1.** Stress-induced mechanophore activation and subsequent chain scission to a thermally remendable polymer.

Figure 2. Mechanical chain scission in PFCB polymers generates trifluorovinyl ether end groups that can be repolymerized thermally.

the extension of such chemistries to material property enhancement remains an important and ongoing challenge.

We became interested in the potential of perfluorocyclobutane (PFCB) mechanophores to fulfill both of the aforementioned functions: cross-reactivity under tension prior to scission and remending following scission. Originally developed by Dow, PFCB aryl ether polymers (hereafter, PFCB polymers or poly-(PFCB)) have been regarded as an important class of polymers for aerospace and electronics due to their low dielectric constant, thermal stability, structural versatility, and tunable properties.[21] They are most commonly prepared through a step growth polymerization mechanism in a thermal $[2\pi + 2\pi]$ dimerization of aryl bis-trifluorovinyl ethers (TFVE), typically at temperatures of between 150 and 200 °C. The dimerization is believed to occur via a diradical intermediate.[22] Because of the nature of their formation, we speculated that PFCB polymers might degrade under force in a way that both creates an intermediate that could potentially be used for force-induced cross-linking or other functionalization, before ultimately fracturing to regenerate the TFVE that could be thermally remended (Figure 2). The underlying hypothesis was that, when placed under tension, cycloreversion back to the reactive TFVE chain ends would predominate as the mechanism of molecular weight degradation. The same net mechanical conversion of PFCB to TFVE has been proposed recently by Cho et al.[23] who observed infrared spectroscopic signatures consistent with such a process in the grinding of solid-state cross-linked polymers, although contributions from local heating, the selectivity for cycloreversion over bond scission, and the stoichiometric efficiency of the proposed healing process were not discussed.

We noted that the success of this vision requires that the mechanism of mechanical degradation differ dramatically from the thermal process, which has been investigated previously. The major thermal decomposition products are hexafluorocyclobutene and phenol,[24] an effectively irreversible reaction that is not suitable for remending or intermediate trapping. Here, we report that both remending and cross-reactivity are possible in response to large mechanical forces. Thermal remending is possible because the products of mechanical degradation differ from those from thermal degradation, instead yielding the desired reactive trifluorovinyl ether end groups. The potential mechanism for stress-induced cross-linking is made possible by the
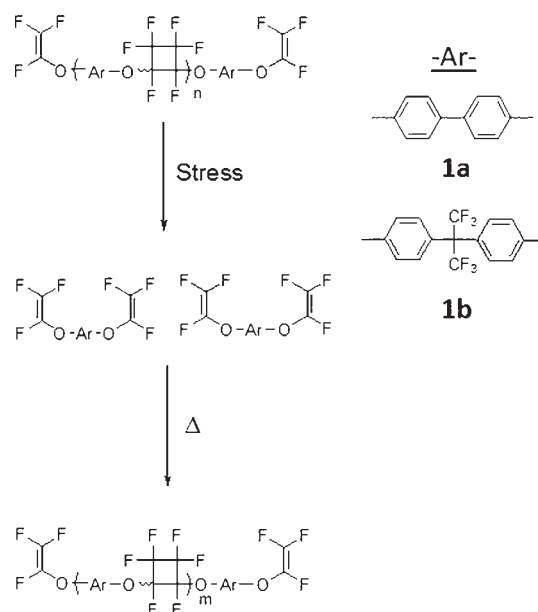
stepwise mechanism of the mechanical reaction, which is revealed to proceed via a diradical intermediate that is reactive to intermolecular addition reactions.

■ RESULTS AND DISCUSSION

We tested our hypothesis in the context of the destructive shear forces generated by pulsed ultrasound, a readily accessible and widely used method of mechanically inducing polymer chain scission and screening for mechanophore reactivity.[2] Sound waves induce the growth and subsequent collapse of bubbles in the solution, causing solvent to flow into the void left by the bubble. This solvent flow has a large extensional shear component, and polymers caught in the shear flow are stretched, leading to forces of tension that are greatest near the polymer midchain. For polymer chains of large enough molecular weight, the forces can lead to chain scission and/or a wide (and growing) range of mechanophore reactivity, including electrocyclic ring-opening reactions,[16,17,25,26] retro-cycloadditions,[18,27] isomerizations,[17,28] and the activation of latent catalysts.[29−31]

Bond scission occurs more readily at some bonds than others in pulsed ultrasound experiments. For example, Encina demonstrated that the rate of polymer chain scission increased when peroxide linkages were incorporated in the backbone of poly-(vinylpyrrolidone),[32] Paulusse and Sijbesma showed that palladium(II) phosphine bonds are selectively cleaved in a linear coordination polymer,[13,14] and Berkowski et al. showed that diazo linkages could be targeted specifically within PEG to extrude N_2.[33] We questioned first whether the scission of the poly(PFCB) was selective for the PFCB functional group, as desired.

When a $\sim$7 mg mL^{-1} solution of **1a** in THF was subjected to pulsed ultrasound for 120 min at 30% amplitude (8.7 W cm^{-2}), the number averaged molecular weight (M_N) of the resulting polymer decreased from 115 to 10 kDa (Figure 3a) (molecular weights are reported as M_N rather than M_W to facilitate both comparisons with NMR data and kinetic fitting of the
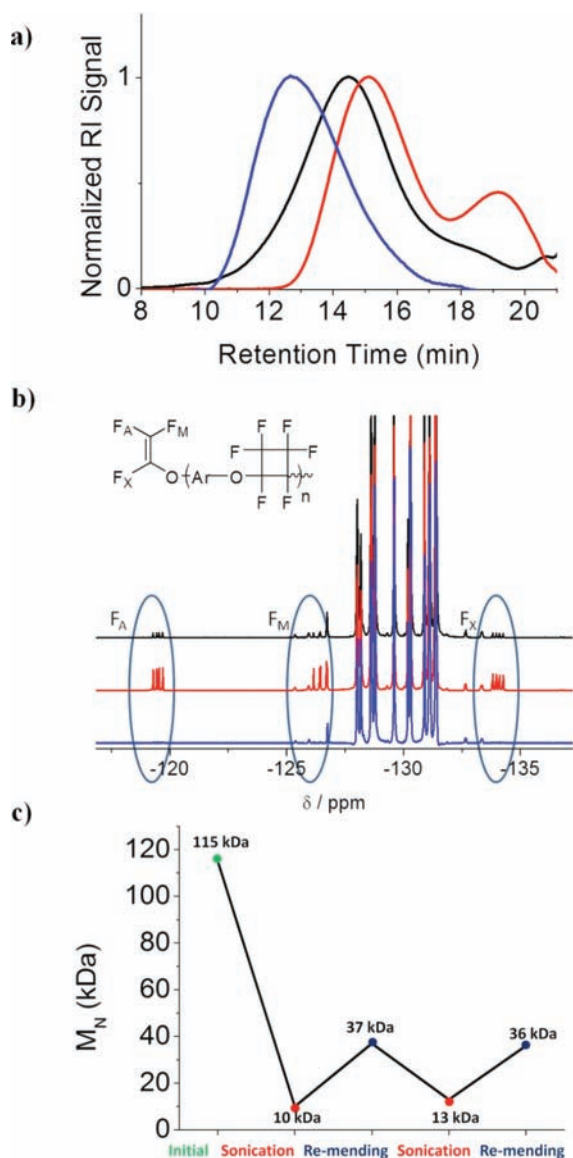
Figure 4. Sonochemical molecular weight degradation of **1a** (black) and **1b** (red) at 7 mg/mL and 30% amplitude. **1a** degrades at a faster rate and to a lower limiting M_N than foes **1b**. The uncertainty in relative M_N is ±5%, based on replicate GPC injections on independent standards. The inset shows the number of bond scission events, normalized to initial number of polymer molecules, as a function of sonication time. The straight line is drawn to show the deviation from linearity.

Because the trifluorovinyl ether groups are formed upon chain scission, the polymer should be able to be thermally remended via the same step-growth polymerization mechanism by which the original polymer formed. The 10 kDa **1a**, generated from the mechanical degradation of the 115 kDa polymer, was heated to 180 °C for 16 h in diphenyl ether (DPE). Thermal remending was confirmed by a combination of GPC-MALS, which showed that the molecular weight had increased to 37 kDa (Figure 3a), and ^{19}F NMR, which showed a concomitant decrease in TFVE content (Figure 3b) and confirmed the mechanism of postscission remending. We point out that the ultimate molecular weight of 37 kDa is typical for these systems; it is known among those in the field that small-scale polymerization of TFVEs is problematic, even for those who are experts in handling these substances, and high molecular weight poly(PFCB), such as the starting material used here, is typically produced only on a large (e.g., kilogram) scale.[35] In our hands, for example, a survey of conditions for the thermal polymerization of 6 kDa **1a** produced in the best case an upper molecular weight of 37 kDa, confirming that the sonicated **1a** behaves indistinguishably from nascent TFVE-terminated prepolymer. Also, when a 37 kDa polymer was sonicated to a molecular weight of 13 kDa (Figure 3c), it was subsequently remended back to 36 kDa, confirming the reversibility of the mechanical degradation.

To determine if the cycloreversion chain scission is unique to the biphenyl polymer, a second polymer with a bis-aryl hexafluoroisopropylidene aryl group, **1b**, was sonicated for 120 min at 30% amplitude. The molecular weight decreased to 18 kDa, and again the ^{19}F NMR spectrum confirms a concomitant increase in TFVE formation. This verifies that **1a** is not unique in its mechanochemical reactivity (see the Supporting Information). The extent of chain scission of **1b** is less than that of **1a** (Figure 4), a difference that might be due to the lower per-weight contour length (and, therefore, higher limiting molecular weight) of **1b** relative to **1a**. Because of the rich structural diversity in PFCB aryl ether polymers that is available through the aryl group, there may be an opportunity to further map the mechanochemical properties described in this Article onto a desired set of thermal and optical properties available within the polymer class.[36]

Figure 3. (a) GPC traces of initial **1a** 115 kDa (blue), sonicated **1a** 10 kDa (red), and remended **1a** 37 kDa (black) polymer solutions. (b) ^{19}F NMR of initial **1a** (blue), sonicated **1a** (red), and remended **1a** (black). (c) A 37 kDa PFCB polymer can be sonochemically degraded and subsequently thermally remended back to 36 kDa. The uncertainty in relative M_N is ±5%, based on replicate GPC injections on independent standards.

degradation profiles).[34] There are multiple possibilities as to where chain scission is occurring during sonication, but the only changes in the ^{19}F NMR spectra correspond perfectly to a drop in the PFCB content and a concomitant increase in the trifluorovinyl ether end groups (Figure 3b); cycloreversion of PFCB is the predominant mechanism of **1a** chain scission. The ^{1}H spectrum tells the same story (see the Supporting Information); the only detectable reaction is from PFCB to TFVE. The 8-fold increase in TFVE content determined by ^{19}F NMR agrees within experimental error with the 6-fold decrease in M_N measured by gel permeation chromatography-multi angle light scattering (GPC-MALS), providing further support that the PFCB is the point of chain scission.
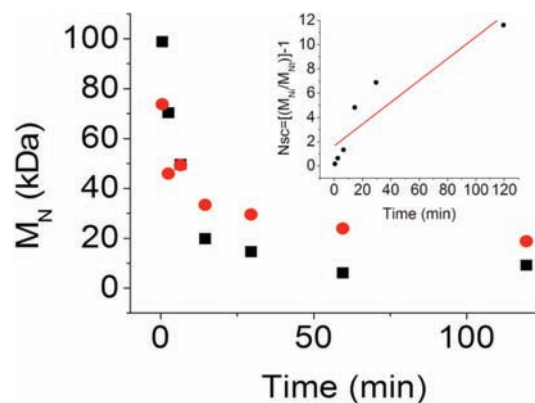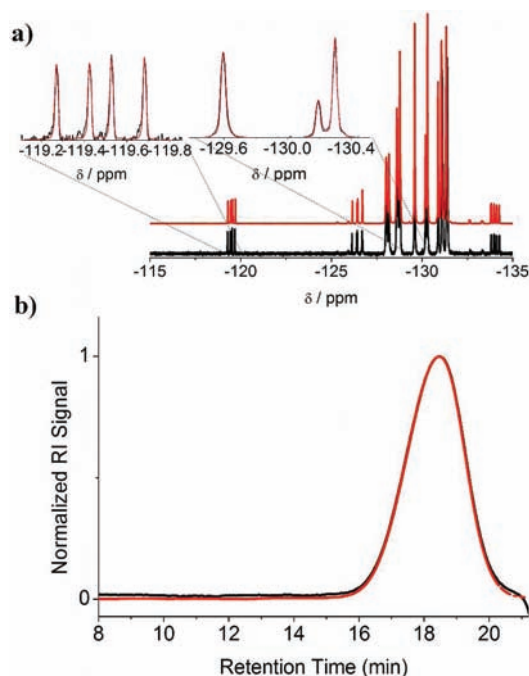
Figure 5. Low molecular weight control experiment for mechanical chain scission. (a) ^{19}F NMR end group analysis of 6 kDa **1a** prior to sonication (black), and after sonication (red) at 7 mg/mL and 30% amplitude for 30 min. (b) GPC traces for initial (black) and sonicated (red) 6 kDa **1a**. No difference in the molecular weight or chemical composition of the initial 6 kDa **1a** polymer is observed.

The mechanical nature of the molecular weight degradation is supported by a few observations. First, the molecular weight profile as a function of sonication time indicates that higher molecular weights degrade more quickly (Figure 4). This includes the presence of an apparent limiting molecular weight at which the degradation "shuts off" or at least slows dramatically, which is indicative of mechanical degradation.[2,37,38] If degradation were independent of molecular weight, as might be expected in a purely thermal process, the number of scission events should increase linearly with time under the conditions explored here, in which the number of intact bonds remains nearly constant (degree of polymerization >10).[39] A plot of number of scission events, $N_{SC} = ((M_n(i) - MW_n(t)) - 1)$ versus time for the sonication experiments clearly deviates from linearity, in particular as the systems nears the limiting molecular weight (Figure 4, inset). Second, the molecular weight dependence was confirmed independently by sonicating a solution of a 6 kDa polymer. This polymer has the same structure as the 115 kDa **1a** but is too small to experience significant mechanical force, and no appreciable degradation was detected either by ^{19}F NMR end-group analysis or by GPC (Figure 5). Third, as mentioned above, the thermal degradation of poly(PFCB)s has been reported to proceed not through reversion to the TFVEs but via elimination of the ethers to give perfluorocyclobutene, and the only new ^{19}F NMR peaks could be conclusively attributed to TFVE. There were no new peaks in the ^1H NMR spectra (see the Supporting Information). Also, to ensure the results were consistent over a range of variables, the sonication power, polymer concentration, and solvent were varied. All three variables are known to affect the rate of molecular weight degradation by pulsed ultrasound.[40,41] Whereas all factors had slight influences on the rate of chain
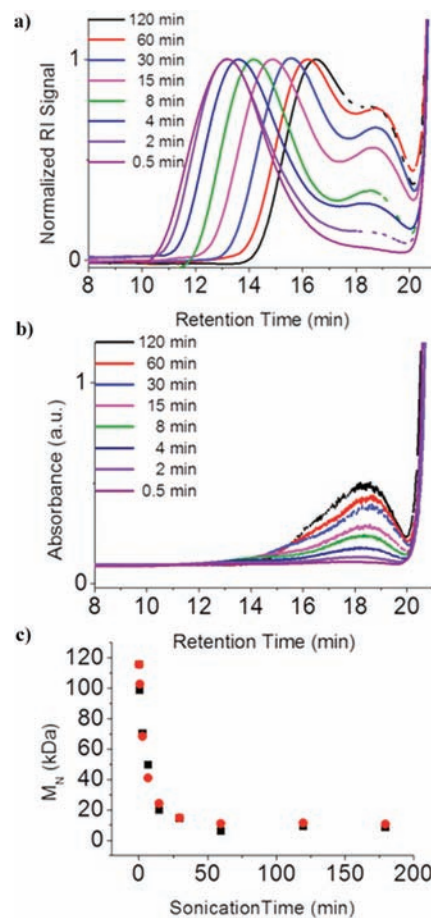

Figure 6. (a) Decreasing molecular weight of **1a**, based on increase in retention time, in the presence of **2**. (b) Increasing $UV_{335 nm}$ signal of **1a** with increasing sonication time in the presence of **2**. (c) Molecular weight degradation of **1a** with increasing sonication time both with **2** (red) and without (black) showing that the presence of **2** does not affect the rate of chain scission.

scission, the sonicated products remained unchanged (see the Supporting Information).

We next investigated the mechanism of the mechanical scission. The thermal conversion of TFVE to PFCB is believed to proceed through a 1,4 diradical intermediate, and we speculated that these same diradical intermediates would form along the polymer main chain during the reverse mechanical process when subjected to pulsed ultrasound, in a manner reminiscent of gDFC mechanophores reported previously.[17,20] Two pieces of experimental evidence support a mechanism in which the mechanically induced PFCB ring-opening proceeds via the formation of a 1,4 diradical intermediate: radical trap addition (Figure 6) and PFCB isomerization.

To test the mechanism of PFCB ring-opening, we first conducted the sonication of **1a** in the presence of 32 mM coumarin−2,2,6,6-tetramethylpiperidine-1-oxyl, **2**, which is known to add efficiently to carbon-centered radicals.[42] As the molecular weight decreased, the $UV_{335 nm}$ signal associated with the lower molecular weight products of chain scission increased (Figure 6a and b), indicating that **2** had added to the polymer backbone. The presence of **2** during sonication did not affect the rate of chain scission (Figure 6c). Mixing **1a** with **2** for 24 h at the same concentrations without sonication resulted in no addition, as did
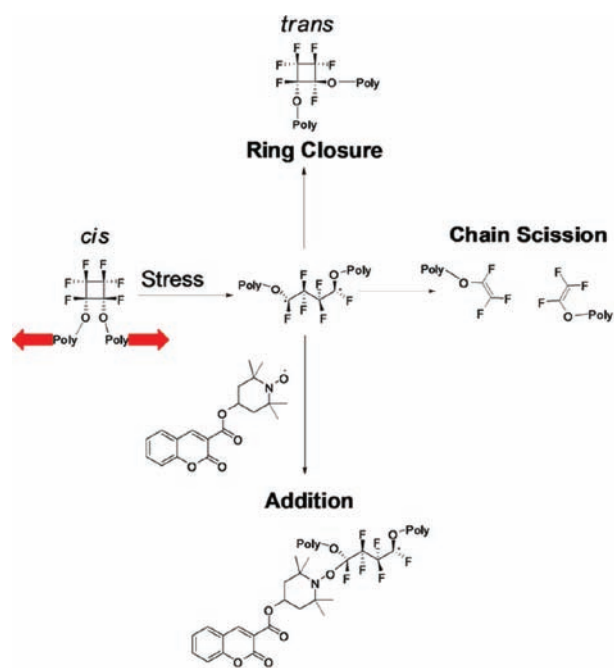
Figure 7. Three outcomes of mechanical activation of PFCB can be attributed to the intermediacy of the 1,4-diradical shown: polymer chain scission to form new TFVE end groups, isomerization upon ring closure (shown here as cis-to-trans, which is the dominant isomerization observed), and radical trap addition to the polymer.

Figure 8. ^{19}F NMR of the PFCB region **1a**. After sonication (black), the peaks corresponding to the trans isomers have increased by 5% when compared to the initial polymer (red).

mixing postsonicated **1a** and **2**. In addition, sonicating the mechanically inactive 6 kDa **1a** with **2** also led to no measurable UV$_{335 \text{ nm}}$ absorbance. Taken together, these control experiments show that the addition of **2** to the polymer backbone is coupled to the application of tension to the polymer, but not to the TFVE product, as expected for the proposed 1,4-diradical intermediate (Figure 7). Quantifying the UV$_{335 \text{ nm}}$ absorbance revealed that, on average, there was 12% incorporation of **2** onto the PFCB polymer following sonication (see the Supporting Information)

Complementary evidence for a diradical intermediate comes from the observation of **1a** isomerization. When trifluorovinyl ether containing monomers are polymerized through cycloaddition, they form a stereorandom PFCB polymer with a cis:trans ratio of roughly 48:52 based on published NMR peak assignments.[43] For a 115 kDa polymer, the total fraction of fluorine in the trans PFCBs is 51% when the TFVE end groups are included. After 30 min of sonication, however, the cis:trans ratio becomes 41:59 with a total trans PFCB content of 56% (Figure 8). The increase in overall trans PFCB content indicates that the changes are not due entirely to the selective scission of cis PFCBs, but instead that some of the cis repeat units are isomerizing to the trans (Figure 8). The reverse isomerization might also be occurring, but the dominant isomerization pathway is from cis to trans. The lower molecular weight fractions, which have presumably undergone more scission events, were collected by preparatory GPC. The initial cis:trans ratios are the same for polymers regardless of molecular weight (an expectation we verified on a 10 kDa polymer; see the Supporting Information), but these repeatedly broken polymers have an even more dramatic final cis:trans ratio of 28:72 and a total trans content of 71%. Interestingly, when the sonicated and unsonicated low M_N polymers were both subjected to the same thermal
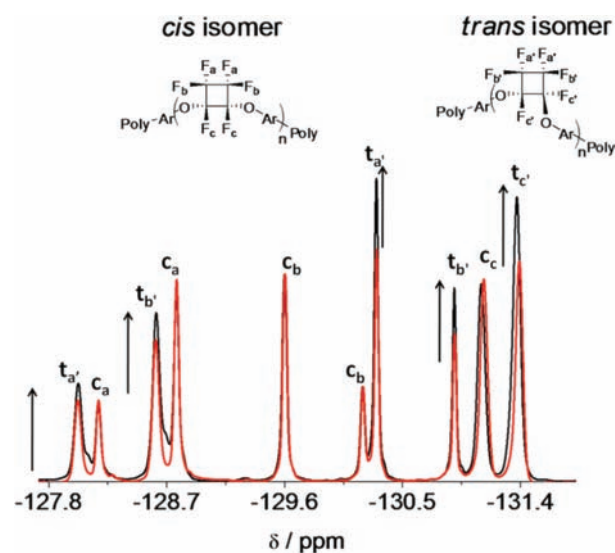
remending conditions, the molecular weights both increased to 37 kDa, and the cis:trans ratio and total trans content remained relatively unchanged from their low molecular weight precursors, further ruling out thermal pathways as a mechanism for isomerization. Isomerization therefore corroborates the presence of a diradical intermediate implicated by **2** trapping.

Recently, our lab reported that when trans polybutadiene functionalized with *g*DFC is sonicated, the *g*DFCs open to 1,3-diradicals under sufficient tension, and preferentially close back to the cis isomer once the tension is removed.[17] Unlike the ring-opening of *g*DFC leading to a 1,3 diradical transition state, which necessarily lasted only as long as the mechanophore is under tension, the 1,4 diradical from PFCB ring-opening is a true intermediate on the force-free potential energy surface of the reaction, meaning that if it is generated by force, it might have a useful lifetime once the force is removed.[17] The presumed longer lifetimes of these diradicals could increase their utility for stress-induced cross-linking or addition reactions. For example, blending a poly(PFCB) polymer with a polymer containing TEMPO repeat units[44] could lead to stress-induced cross-linking/strengthening. The amount of PFCB ring-opening is difficult to quantify, but the increase in trans content means that multiple PFCBs are opened on the time scale of one scission event. From the data, we cannot determine whether the cis PFCB opens more easily than the trans isomer, or if the diradical formed mechanically is more likely to close to the trans (presumably once the force is released) than the diradical formed during thermal polymerization. On the basis of the prior *g*DFC work,[17] however, the former seems more likely.

■ CONCLUSION

When PFCB polymers are mechanically degraded by pulsed ultrasound, the products are different from those of thermal degradation. The point of chain scission is the PFCB moiety, resulting in a cycloreversion to TFVE. Because there are multiple PFCB units along each polymer, multiple mechanophores are activated during the chain scission, as evidenced by radical trapping experiments and the observation of isomerization

within the polymer. When a PFCB mechanophore is opened under tension, a 1,4 diradical is formed, making stress-induced cross-linking a possible pathway for self-healing. Also, the stress-induced isomerization, from cis to trans, is a possible mechanism for molecular stress relief[45] due to the increase in contour length of the stress-activated polymer subchain (in the absence of scission). Finally, due to the nature of the mechanical chain scission, the PFCB can be remended at elevated temperatures.[23] This thermal remending is similar to that of other retro-Diels—Alder chain scission mechanisms,[9,18] but is shown here to proceed through a reactive intermediate that can participate in intermolecular radical addition reactions. The PFCBs therefore possess what is, to the best of our knowledge, a unique combination of properties: the potential for localized, stress-induced cross-linking and a thermal remending "failsafe". The broad utility, structural diversity, and high mechanophore density make PFCB polymers good candidates for stress-responsive materials, spawning our ongoing interest into the consequences of these properties in the solid state, along the lines originally proposed by Cho et al.[23]

EXPERIMENTAL SECTION

Materials. Inhibitor-free tetrahydrofuran (THF), diphenyl ether (DPE), and methanol were all purchased from Aldrich and used without further purification. Perfluorocyclobutane (PFCB) polymers **1a** and **1b** were both donated and purchased from Tetramer Technologies LLC, and coumarin—2,2,6,6-tetramethylpiperidine-1-oxyl (**2**) was synthesized according to published reports.[17]

Sonication Experiments. Each sonication was performed in a three-armed Suslick reaction vessel at varying concentrations of polymer solutions in ~15 mL of inhibitor-free THF. The solutions were deoxygenated with bubbling N_2 for 30 min prior to sonication. The temperature was kept between 6 and 9 °C in an ice—water bath, and the sonication pulse sequence was set to 1 s on/1 s off. Samples for GPC analysis were taken from the vessel and injected directly. After sonication was complete, the polymers were precipitated from a concentrated solution with methanol, washed with methanol, and dried in a vacuum desiccator prior to ^{1}H and ^{19}F NMR analysis.

Remending. Thermal remending experiments were conducted at varying polymer concentrations in DPE. The flask was wrapped with foil to exclude light. The polymer solution was degassed by three successive freeze/pump/thaw cycles, and the flask was then placed in an oil bath at 180 °C with rapid stirring.

Radical Trapping. To investigate tension induced ring-opening of the PFCB moieties, an inhibitor-free THF solution of ~7 mg/mL of **1a** and 32 mM of **2** was sonicated at 30% amplitude. Aliquots were removed at time intervals, and the aliquots were analyzed by GPC with an in-line UV detector to determine the amount of **2** incorporation.

ASSOCIATED CONTENT

S **Supporting Information.** NMR, GPC, UV characterizations, control experiment details, and additional details. This material is available free of charge via the Internet at http://pubs.acs.org.

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