The molecular mechanism of constructive remodeling of a mechanically-loaded polymer

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Large or repeated mechanical loads usually degrade polymers by accelerating fragmentation of their backbones but rarely, they can cause new backbone bonds to form. When these new bonds form faster than the original bonds break, mechanical degradation may be arrested or reversed in real time. Exploiting such constructive remodeling has proven challenging because we lack an understanding of the competition between bond-forming and bond-breaking reactions in mechanically-stressed polymers. Here we report the molecular mechanism and analysis of constructive remodeling driven by the macroradical products of mechanochemical fragmentation of a hydrocarbon backbone. By studying the changing compositions of a random copolymer of styrene and butadiene sheared at 10 °C in the presence of different additives we developed an approach to characterizing this growth/fracture competition, which is generalizable to other underlying chemistries. Our results demonstrate that constructive remodeling is achievable under practically relevant conditions, requires neither complex chemistries, elaborate macromolecular architectures or free monomers, and is amenable to detailed mechanistic interrogation and simulation. These findings constitute a quantitative framework for systematic studies of polymers capable of autonomously counteracting mechanical degradation at the molecular level.
Mechanical load accelerates fragmentations of polymer chains, degrading its properties\(^1-6\). A popular chemical approach to reversing this damage is to control the products of such fragmentations by incorporating mechanochromically labile bonds into common polymer backbones\(^7-13\). Once the load is removed, bimolecular additions of pairs of the resulting fragments, usually upon energy input in the form of heat, irradiation or reactants, generates many (but not all\(^1\)) failed relatively labile backbone bonds. Despite numerous impressively clever proof-of-the-concept demonstrations, practical implementations of this approach face considerable barriers. Incorporating dissociatively labile bonds into polymer backbones necessarily affects the mechanical properties (which may be partially ameliorated by including such bonds into chain loops\(^15,16\)) and processibility of the polymer\(^5\), increases costs and complicates synthesis.

The alternative to healing the damage after it occurred is to form new backbone bonds in the loaded material fast enough for the size of the average chain to remain constant or grow despite simultaneous competing mechanochemical chain fracture. Such constructive remodeling\(^8,17,18\) is a potentially effective approach to autonomously reinforcing overstressed volumes of the loaded material that are at the highest risk of failure. Its only known demonstration relied on forming new bonds away from the sites of chain fracture in a sheared mixture of a polymer of dibal-cyclopropane (DHC) and a small-molecule bifunctional crosslinker\(^18\). Mechanical load accelerated isomerization of DHC monomers to allylic halides that combine spontaneously with one terminal group of the small-molecule crosslinker. Unlike the covalent rebonding approach above, no mechanically fractured bond was regenerated, and the new bonds formed irreversibly. The resulting crosslinking kinetics is largely uncontrollable (although a partial work-around was demonstrated in solution\(^19\)):

- at the onset of the remodeling, the concentration of isomerized monomers is high and new bonds form much faster than mechanochemical bond scission, causing embrittlement. As either reactant is depleted, crosslinking can no longer compensate bond fracture and the material degrades as usual.

The above analysis suggests that enabling spontaneous backbone bond formation to outcompete mechanochemical bond scission is a necessary but insufficient requirement to realize practical constructive remodeling. We identify at least 4 additional requirements. First, it doesn’t require mechanochromically labile backbone bonds. Second, it generates backbone bonds that are as chemically indistinguishable from the lost bonds as possible, to avoid the problem of reactive-group depletion. Third, it forms new bonds both between products of chain fracture and between intact chains, to rapidly grow the average chain (or increase the crosslinking density) in overstressed volumes. Fourth, the number of new bonds formed per fractured bond is independent of the degree of remodeling and tunable by changes in the polymer composition and/or microstructure to yield stable remodeling behavior adjustable to the anticipated loading profiles the material will experience during use.

The above considerations suggests that the abundance of simple C–C bonds in backbones of synthetic polymers\(^20\) makes spontaneous regeneration of simple C–C backbones in a mechanically stressed polymer a particularly attractive target for constructive remodeling. When overstretched, a C–C backbone bond usually homolyzes to a pair of macroradicals\(^12,21\). Such mechanochemically generated macroradicals were previously used as macronitiators of radical polymerization of styrene or acrylates\(^9,22-24\), which forms new backbone bonds. Whereas swelling polymers with a monomer or decorating them with pendant acrylate or styrene groups is impractical, a number of polymers already in commercial use, exemplified by polybutadiene, have either backbone or pendant olefin C–C bonds. In theory, such polymers could serve as a starting point for integrating constructive remodeling into existing and emerging engineering materials. In practice, we lack an understanding of the factors that control the rates of spontaneous regeneration of simple C–C backbones under mechanical load or the tools to enumerate these factors. The present study is a first step to filling this knowledge gap.

Unlike the more reactive C–C bonds of acrylates or styrenes, few examples of uncatalyzed condensed-phase radical polymerizations of unconjugated C–C have been reported, or studied mechanistically\(^25\). The reaction is slow and only short kinetic chain lengths have been achieved in solids even at >100 °C\(^26\). Heating certain polybutadienes or styrene/butadiene copolymers in the presence of an organic peroxide creates up to 20 crosslinks per oxide molecule, presumably by addition of chemically-generated macroradicals to the vinyl groups of the adjacent chains\(^27\). However, other unsaturated polymers, including polyisoprene, neoprene and many butadiene copolymers only produce (sub)stoichiometric amounts of crosslinks. Crosslinking by addition of a macroradical to a backbone C–C bond was also proposed in unsaturated polyolefins at >70 °C\(^28,29\) but the number of new bonds per macroradical is unknown and likely sub-stoichiometric. Conversely, macroradical recombinations, not additions to sp\(^2\) C atoms, are thought to dominate polymer crosslinking in reactive melt processing\(^26,30\) and in polyolefins under y irradiation. Finally, in ball milling of unsaturated polyolefins, such as polyisoprene, or their mixtures with saturated polymers the new bond formation, evident by chain grafting, is always accompanied by a reduction in the average chain size, suggesting that chain fracture dominates\(^21,23\).

Although these examples suggest that olefinic C–C bonds may support spontaneous formation of new backbone C–C bonds without the need for free monomer, they tell us little about whether such bond formation can outcompete bond loss by chain fracture, which is the minimum requirement of constructive remodeling. Biasing this competition towards bond formation is more challenging in a mechanically-stressed than in a heated polymer because the susceptibility of a chain to fracture mechanochemically scales much more steeply with chain size\(^2\) and the degree of branching\(^31\) than thermal chain scission. In other words, the large and topologically complex products of addition of macroradicals to surrounding chains are proportionally more likely to fracture when overstretched than heated. No existing knowledge allows the effect of the resulting mechanochemical feedback loops on the remodeling kinetics to be estimated even qualitatively.

Molecular mechanisms of mechanochemical remodeling of bulk polymers have been little studied, which means that the field lacks consensus protocols that govern the design of such studies or interpretations of their results. Here we adopted a physical organic approach\(^32\), combining experiments, quantum-chemical calculations and mechanistic microkinetic simulations, to enumerate and validate the simplest mechanism responsible for changes in the composition and microstructure of random styrene/butadiene copolymer under steady-state shear. Our results demonstrate that constructive remodeling based on radical oligomerization of low-reactivity unconjugated C–C bonds, initiated by mechanochemically generated macroradicals, is both feasible under practically relevant conditions and mechanistically tractable at the molecular level.

**Results**

We chose to study the mechanism of regeneration of C–C backbones in sheared random copolymer of butadiene and
Fig. 1 The styrene-butadiene copolymer and radical scavengers. The sheared polymer had $T_g = -35^\circ C$ and contained $30.5 \pm 0.5%$ and $27.1 \pm 0.7%$ by mass of styrene (blue) and 1,2-enchained butadiene (green), respectively, with the rest being 1,4-enchained butadiene (red), as determined by NIR spectroscopy (Supplementary Fig. 1). AH represents a class of antioxidant additives routinely used for protection of commercial polymers against thermoxidative ageing. $^{38,39}$ $A^*$ is a radical scavenger produced in situ when a macroradical abstracts phenolic hydrogen atom from AH. $T^*$ combines a well-established radical trap $^{40}$ (TEMPO) with pyrene, whose characteristic absorption spectrum allows simple and accurate spectroscopic quantitation of the number of $T$ moieties bound to a polymer chain. Bulk concentrations of AH and $T^*$ used in a subset of our experiments are also listed.

Experimental results

All experimental results discussed here are for samples of identical mass distribution ($M_n = 151 \pm 5$ kDa, $M_w = 165 \pm 2$ kDa) sheared at $10^\circ C$ to minimize thermal remodeling; see Supplementary Fig. 7 and accompanying text for a brief discussion of the results at other temperatures and for other initial mass distributions. Each sample was repeatedly passed through a $1 \times 10$ mm (dia. $\times$ length) capillary at a constant velocity and frequency in either nitrogen atmosphere or dry air (see Methods and Supplementary Information for further details). We continuously recorded the applied force (Supplementary Fig. 6) and periodically sampled the material for analysis by size-exclusion chromatography (SEC) and spectrophotometry. In addition to neat copolymer, we sheared samples containing a dissolved radical scavenger, $T^*$ (at 10, 20 and 100 mM for anaerobic experiments and 20 mM for aerobic shearing, Fig. 1) and a common antioxidant additive, AH (at 20 mM for anaerobic and 20 and 200 mM for aerobic experiments). $T$-containing samples allowed us to understand the relative contributions of chains of different mass and topology to remodeling kinetics. We quantified the effects of $O_2$ and the antioxidant (AH) on the remodeling mechanism because constructive remodeling needs to operate in the presence of either soluble to be practical. In our experiments the concentration of AH was up to 20 times greater than that used in commercial polymers to maximize its mechanistic effects. Because chain/chain additions produce complex mixtures of chains of different topology, the true mass distribution of a sheared material is accessible only from simulations$^{41}$ as described below. Here all reported measured molar masses are apparent: for linear chains, the true and apparent masses are identical, whereas branched chains of the same hydrodynamic radius have the same apparent mass irrespective of their microstructures and masses.

Apparent molar mass distributions (aMMDs) of sheared samples demonstrate accumulation of chains with masses both smaller and larger that the initial chains under all studied conditions (Fig. 2a and Supplementary Fig. 10), suggesting that chains both fracture and the resulting macroradicals add to surrounding chains. In all samples the distribution of the low-mass product fraction was centered at the mass approximately half that of the initial sample, as is commonly observed in bulk samples under diverse loads$^{1,2}$. Compared to anaerobically sheared neat copolymer, changes in the apparent weight-average mass, $M_w$, of all other sheared samples (Fig. 2b) along with their bifurcated aMMDs (Supplementary Fig. 15) suggest that $O_2$, $T^*$, and AH suppress but do not eliminate the C-C bond regeneration even at the highest concentrations employed (0.1 and 0.2 M for $T^*$ and AH, respectively).

Transient generation of macroradicals in aerobically-sheared samples is suggested by the accumulation of chain-bound hydroperoxy (OOH) groups, whose concentrations we quantified by iodometry$^{42,43}$. Conversely, hydroxy or carbonyl groups which accumulate in aerobically heated polyolefins$^{44}$ by thermal decomposition of hydroperoxidized chains were undetectable. AH reduced chain peroxidation ~10-fold at 20 mM and 60-fold at 200 mM. We could not quantify the concentration of OOH moieties in aerobically-sheared T-containing samples because of the interference from residual $T^*$.

Shearing samples containing dissolved $T^*$ incorporated T moieties into polymer chains, as evidenced by the appearance of the pyrene absorption in UV-vis spectra of SEC fractions primarily at apparent masses smaller and larger than those of the intact sample. By deconvoluting the spectrum of each fraction into that of styrene and pyrene (Supplementary Fig. 15), we estimated the average number of T moieties per styrene for all chains of the same apparent mass. The total concentration of these moieties, $[T_{poly}]$, scaled linearly with the number of shearing cycles. In contrast to the accelerated loss of $M_w$ in samples with higher bulk T concentrations, $[T]_{bulk}$, the accumulation rate of $[T_{poly}]$ was independent of $[T]_{bulk}$, but slowed by $O_2$ (Fig. 2c: green, magenta and blue lines vs. brown line). This suggests that under $N_2$, $T^*$ binding is the dominant sink of macroradicals at all $[T]_{bulk}$ studied, whereas $O_2$ enables additional radical-destroying reactions. Negligible addition of macroradicals to pyrene of $T^*$ is evidenced by the total pyrene absorption of sheared samples remaining constant throughout shearing.

The remodeling mechanism from DFT computations. Fragmentation of a polymer chain produces an intractable mixture of structurally distinct macroradicals. Reactions of these macroradicals with other chains or small-molecule solutes further increase the number of species. To reduce this complexity, we calculated the reaction and activation enthalpies, $\Delta H^r$ and $\Delta H^a$, respectively, of H-atom transfer and addition to sp$^2$-C atoms for representative pairwise combinations of short copolymer and...
macroradicals (Supplementary Tables 4–7). The results confirmed that the reactivities of all macroradicals plausibly formed in mechanically loaded copolymer can be represented by two species: ar* that includes all alkyl radicals and sr* (for stabilized radicals) that includes all allylic and benzylic radicals (Fig. 3). The results were broadly consistent across the 6 functionals we tested (Supplementary Table 3), with the numbers cited throughout the main paper are at the uMPW1K/G(d) level. Calculated ΔH° and ΔH‡ for either addition or abstraction vary by <2 kcal/mol among radicals of the same type regardless of their size, branching, or the internal vs. terminal location of the unpaired electron. All calculated ΔH° and ΔH‡ of ar* reactions are less than those for equivalent sr* reactions by >15 and ~5 kcal/mol, respectively (Supplementary Tables 3, 4), consistent with the known differences between alkyl and stabilized (allylic/benzylic) radicals.

The fraction of ar* in the fragmentation products of the copolymer was calculated to increase monotonically with fracture force before plateauing at ~50% for ~4.2 nN (Supplementary Fig. 20a). The chain fracture force(s) in a sheared material are unknown. However, they must be high enough to reduce the half-life of the overstretched backbone to (much) less than the residence time of the chain in the capillary (1.6 s) and its terminal relaxation time (~10 s, see SI for further details), because otherwise, the chain will relax before fracturing. At 10°C and τh < 1.6 s, the average chain fracture produces 0.8–0.98 ar* on average.

Based on these results we identified 4 generic reactions (r1–r3 and r6a, Fig. 3) that constitute the simplest mechanism of mechanochemical remodeling of neat copolymer under N2. Mechanochemical chain scission (r1, red arrow) yields a pair of shorter macroradicals, sr* and ar*, thus reducing the average chain size and the number of backbone bonds. A new backbone C–C bond is formed whenever aR* adds to a random non-aromatic sp² C (either backbone or pendant) of an adjacent chain (P), yielding a larger and more branched alkyl radical, aR* (r2, blue arrow). The resulting ar* continues to accrete P chains sequentially until it abstracts an allylic or benzylic H atom from an adjacent chain (r3, magenta arrow), creating internal sr* and itself becoming P, or when it recombines with another ar* or sr* (r6a, green arrow). Addition of sr* to an sp²-C atom requires traversing considerably higher activation barrier than that of ar*, so that in the absence of an exogenous reactant, the main sink of sr* is macroradical recombinations (r6a, green line).

The presence of A*, T* or O2 enables additional reactions. Our calculations suggest, in accord with previous experimental and computational data, that all macroradicals bind A*, T* or O2 at diffusion-limited rates (Supplementary Table 14), which are determined both by the molecular size of A*, T* or O2 (Supplementary Table 14) and their concentrations. Binding of T* or A* to a macroradical (r6b) yields closed-shell products whose reactivity is qualitatively identical to that of the initial chain, P. These reactions compete with additions of ar* to P (r2) and...
with recombinations of macroradical pairs, reducing the average size of remodeled P, which is indeed observed. Another reaction that can terminate aR• growth is H atom transfer from AH (r4, orange), which is the primary source of A• in the absence of O2.

Diffusion-limited binding of O2 to sR• or aR• yields peroxy radicals, ROO• (r5)49, whose reactivity is, according to our calculations, independent of the nature of R (Supplementary Table 5) and distinct from that of C-based radicals in at least three important aspects. First, ROO• has no affinity for O2 or A• and is rapidly reduced by T•50. Second, unlike aR•, ROO• kinetically favors H atom abstraction (r3) over addition to sp2-C atoms (r2). Third, the relatively slow addition of ROO• to sp2 C yields a radical that undergoes spontaneous irreversible O–O bond homolysis to regenerate chains of the original size and microstructure faster than the addition rate (Supplementary Tables 5, 10, 11, and ref. 49). Consequently, addition of ROO• to sp2 C atoms is expected to have no observable manifestations and is omitted from our mechanism.

Mechanistic microkinetic simulations. We confirmed that the mechanism in Fig. 3 reproduces quantitatively all available experimental data using kinetic parameters whose values are close to those calculated by DFT. To do so we simulated the evolution of both the composition and topology of each polymer chain comprising the remodeling sample, which is more informative than fitting a putative mechanism to either the observed apparent MMD or the bulk composition only, as has been standard in the field. For example, apparent time-dependent MMDs of a polymer that undergoes competing non-mechanochemical chain fracture and crosslinking were simulated using a simple empirical mathematical expression without defining the underlying reaction mechanism54. Such an approach obviously cannot demonstrate that a mechanism reproduces the experiments51. Conversely, the reported mechanistic simulations attempted to reproduce only

Fig. 3 The simplest mechanism of low-temperature mechanochemical remodeling of neat and doped copolymer under N2 and air. P is any closed-shell copolymer chain regardless of microstructure, size or functional groups.
the total concentrations of certain functional groups while ignoring how these functional groups were distributed among chains of different masses or and to simulate only apparent time-dependent $M_n$ or $M_w$ rather than the full MMD. This alternative is equally unsuitable for a mechanochemically remodeling polymer because chains of different size and topology are characterized by vastly different susceptibilities to fracture when overstretched. The other advantage of our simulations is the detailed description of the distribution of chain sizes and topologies in the remodeling samples that it yields.

To make keeping track of tens of thousands of chains of unique mass and topology that comprise a remodeling polymer tenable, we exploited simple relationships between the size and contour length of each chain and its reaction probabilities to define the tens of thousands of microscopic rate constants that describe the kinetics of each unique chain using just 12 independent kinetic parameters. First, we relied on a previously established set the rate constant for mechanochemical fragmentation of the most abundant chain in the intact polymer (150 kDa), $k^{ref}_{\sigma}$, to the middle of the stretched segment (e.g., Supplementary Eq. (14)). Second, we incorporated a common assumption that each C=C bond in a macromolecule reacts independently, which means that the probability of a chain to add an aR$^*$ macroradical is proportional to the chain mass. The same applies to an H atom transfer to an aR$^*$ radical (e.g., Supplementary Eq. (16)). Finally, we assumed that the reactivity of either aR$^*$ or sr$^*$ macroradicals is independent of their size or microstructure as suggested by the DFT calculations described above.

Because the mechanism in Fig. 3 is independent of the overall rate of the material remodelling on the laboratory timescale we set the rate constant for mechanochemical fragmentation of the most abundant chain in the intact polymer (150 kDa), $k^{ref}_{\sigma}$, to 1 and expressed all other rate constants (Supplementary Table 18), and the remodeling time as multiples of $k^{ref}_{\sigma}$. We systematically varied the rate constants along with the chain-fragmentation parameters, $m$ and $\sigma$, to reproduce measured $aM_w$ as a function of the concentration of either polymer-bound T or OOH, $[X_{poly}]$, Fig. 4a. These correlations also yielded the absolute values of $k^{ref}_{\sigma}$ for neat and AH-doped copolymer sheared in air, and T-doped copolymers sheared in N$_2$ and air. The small variations of $k^{ref}_{\sigma}$ across this range of conditions (average $k^{ref}_{\sigma} = (4.7 \pm 0.8) \times 10^{-4}$ cycle$^{-1}$, Supplementary Fig. 29) is consistent with the hypothesis that mechanochemical kinetics in flows is primarily determined by the local strain rate, which is identical in all our experiments and independent of the extent of remodelling. We used these absolute $k^{ref}_{\sigma}$ to confirm that the simulations reproduced measured $aM_w$ vs. shearing cycles correlations of anaerobically sheared neat and AH-containing polymers (Fig. 4b). These conditions did not generate detectable chain-bound species and therefore lack $[X_{poly}]$ vs. $aM_w$ correlations of the other samples. Our simulations also reproduced the measured distributions of both the apparent chain masses, $aM_w$, and polymer-bound T moieties, $T_{poly}$ (4c-f and Supplementary Figs. 24, 25). We used a combination of measured and fitted contraction factors to convert true chain masses in simulations to measured apparent masses.

The relative rate constants that reproduced the experimental correlations were comparable to the corresponding $\Delta$AH$^*$ from DFT calculations, with the biggest difference of $\sim 3$ kcal/mol for the relative rate constants of H-atom abstraction by ROO$^*$ vs. aR$^*$. This suggests that the mechanism in Fig. 3 reflects the intrinsic reactivities of macroradicals and sp$^2$ carbons, and is not specific to the loading mode used in this study. Such conclusion is further supported by the existing literature demonstrating that the same polymer produces the same macroradicals in different mechanical loading scenarios, including grinding, uniaxial compression of a bulk sample, freeze-fracture, phase transition, and sonication in solution. It also suggests that using relative rate constants from DFT calculations can predict the evolution of the composition of the loaded material accurately enough to reduce the need for measurements.

**Key mechanistic findings.** The data described above is consistent with the formation of new backbone C=C bonds in all mechanically loaded samples. The simulations confirmed that in neat copolymers under N$_2$ or air and in AH-doped copolymer under N$_2$ the mass of the average chain, $M_n$, increases during shearing and the number of newly formed backbone bonds per chain fracture, $\nu$, exceeds 1 (Fig. 5a). In other words, the remodelling is constructive. In all other loading conditions the new backbone bond formation reduced the extent but didn’t reverse mechanical degradation, as evidenced by the corresponding $M_w$ values being below that of the intact sample, $M_w^*$, but exceeding $M_n$ for the polymer in a dilute sonicated solution, where no backbone bonds reform ($\nu = 0$, dotted line). These examples illustrate the point made in the introduction: a spontaneous bond formation doesn’t guarantee that an average chain of a loaded sample grows, i.e., that the remodeling is constructive instead of degradative.

In all samples, the competition between bond homolysis and regeneration creates mixtures of linear low-mass (LLM) and branched high-mass (BHM) chains (Fig. 5b and Supplementary Fig. 31). Analysis of the $[T_{poly}]/[styrene]$ ratios as a function of mechanical degradation, as evidenced by the corresponding $M_w$ values being below that of the intact sample, $M_w^*$, but exceeding $M_n$ for the polymer in a dilute sonicated solution, where no backbone bonds reform ($\nu = 0$, dotted line). These examples illustrate the point made in the introduction: a spontaneous bond formation doesn’t guarantee that an average chain of a loaded sample grows, i.e., that the remodeling is constructive instead of degradative.

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sequential intramolecular additions and/or H-atom shifts (Supplementary Table 8). We cannot yet distinguish between chain-diffusion and radical-diffusion recombination mechanisms because they yield similar distributions of chain sizes and degrees of branching.

Exogenous reactants (T•, AH, O2) decrease ν by competing for aR•, reducing the average size and steady state concentration of these actively growing radicals. Because the rate of macroradical recombinations scales quadratically with their concentration, the contribution of such recombinations to the average chain size is particularly sensitive to the presence of chain-terminating additives. For example, the largest chains in neat copolymer result from recombination of pairs of aR• radicals; all additives completely eliminate this path, but they affect aR• + sR• recombinations differently. T• eliminates them by capturing sR• quantitatively, thereby increasing the yield of LLM chains per fracture. Conversely, the negligibly slow reaction of AH with sR• increases the relative importance of aR• + sR• recombinations, which enriches the remodeling mixtures in 3- and 4-arm star chain at the expense of larger BHMM congeners. This ability to control the distribution of chain topologies by using an additive with different kinetic selectivities towards the macroradicals of

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**Fig. 4** The proposed remodeling mechanism reproduces all experimental observations. a Experimental (dots) and simulated (lines) correlations between the concentration of polymer-bound T or OOH moieties, [Xpoly], and change in aMw; b Experimental (dots) and simulated (lines) increase in aMw as a function of the number of shearing cycles for the conditions that do not generate polymer-bound T or OOH moieties. Error bars define 2σ confidence intervals. Representative experimental (c) and simulated (d) differential aMMDs at the end of each shearing experiment. Each differential aMMD was scaled to the same minimum value to facilitate comparisons. See Supplementary Figs. 25 and 23 for all simulated and apparent true MMDs. Distribution of polymer-bound T moiety per styrene, [Tpoly]/[styrene] as a function of the apparent chain mass at the end of each listed experiment (e), and the corresponding simulated distribution (f). Because larger chains contain more styrene moieties per chain, the approximately constant [Tpoly]/[styrene] vs. mass correlations at >200 kDa correspond to increasing numbers of T moieties per average chain: for example, an average 400 kDa chain with [Tpoly]/[styrene] = 3 × 10⁻³ carries 4.7 ± 0.4 T moieties (Supplementary Fig. 32).
Fig. 5 Key findings and predictions of the mechanism. 

a The molar mass of the average chain relative to that of the starting material, $M_n/M_0$, as a function of the mass fraction of remodeled material; $\nu$ is the number of backbone bonds formed per fracture.

b The composition of the product chains at different polymer compositions. c The primary reactions responsible for repeated formation and fracture of branched chains in the mechanically loaded polymer. H-atom transfers are omitted. Chain fragmentation always yields two macroradicals; when they have the same microstructure, only one chain is shown for simplicity.

d Reaction selectivities of $sR^*$ in polymers of different composition. Relatively slow diffusion in the solid allows additions (blue) to compete with barrierless recombinations with T, A* or O2 (green and grey). The equivalent data for $aR^*$ and ROO$^*$ is plotted in Supplementary Fig. 28.
different types represents a potentially valuable design tool to control the course of remodeling. Chain growth remains detectable even at highest \( T^* \) _brain_ employed (Fig. 5d) thanks to the relatively slow diffusion of even small-molecule solutes in the polymer and the very fast addition of \( \text{AR}^* \) to adjacent chains thanks to low \( \Delta H^f \) (\( >9.5 \text{ kcal/mol} \), Supplementary Table 4) and high concentration of sp²-carbons (Supplementary Table 9).

Unlike \( T^* \) and AH, \( O_2 \) doesn’t reduce the total concentration of macroradicals, and the distinct patterns of remodeling in \( N_2 \) and air reflect rapid binding of \( O_2 \) to \( \text{AR}^* \) and \( \text{SR}^* \) and the kinetic preference of resulting \( \text{ROO}^* \) for H-atom abstraction over addition (Fig. 5d and Supplementary Fig. 28). In the absence of antioxidants, conversion of \( \text{ROO}^* \) to \( \text{P_OOH} \) by H abstraction increases the flux of \( \text{SR}^* \) (r4, Fig. 3), which allows peroxidation of another chain, eventually yielding 3.9 chain-bound OOH moieties per chain fracture. A comparable yield was speculated to characterize low-temperature radical polymerizations in the presence of \( O_2 \) traces. In both cases, \( \text{P_OOH} \) chains accumulate because they are inert at the respective reaction temperatures. AH reduces the peroxidation yield because diffusion-limited H-atom transfer from AH to \( \text{ROO}^* \) suppresses regeneration of \( \text{SR}^* \). The concomitant increase in the \( A^* \) flux, which adds rapidly to \( \text{AR}^* \) but is inert to \( \text{ROO}^* \), makes AH nearly as effective at inhibiting chain growth in air as \( T^* \) (Fig. 5d). Consequently, effective suppression of chain peroxidation while maximizing constructive remodeling requires minimizing \( O_2 \) concentrations in the overstressed volumes of material.

Importantly for prospective applications of macroradical-driven constructive remodeling, \( O_2 \) does not accelerate degradation of the loaded polymer, in contrast to thermal oxidation of polyolefins, which often demonstrate self-accelerating kinetics. The reason is the strong kinetic selectivity of \( \text{ROO}^* \) towards H atom abstraction over any other reaction, including recombination, thanks to low \( \Delta H^f \) and the abundance of allylic and benzylic H atoms in the copolymer. H atom abstraction yields a peroxidized chain, \( \text{P_OOH} \) (r4, Fig. 3), whose thermal and mecha

### Discussion

The data above demonstrates autonomous regeneration of backbone bonds in a loaded polymer initiated by macroradical products of chain fracture without the limitations inherent to any previously demonstrated strategy of achieving constructive remodeling, such as the use of mecha

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\text{v} = \frac{\text{n}}{\text{M}_n} \times 10^6
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intractably many structurally unique components, each with distinct kinetic and thermodynamic stabilities. Accounting for all this diversity is neither feasible nor necessary because the differences between many such components are simply undetectable and lack practical or conceptual significance. Consequently, a useful mechanism of a reacting polymer is predicated on identifying a logical, internally consistent and ideally generalizable strategy for reducing this complexity (coarse-graining61). Here we described a twofold approach. First, the mechanism in Fig. 3 identifies the subset of reactions that we propose are primarily responsible for remodeling under shear. This mechanism enables both qualitative discussions of the chemistry that underlies remodeling and systematic building of reaction networks needed for quantitative simulations of the evolving composition of a remodeling sample. Second, we assumed that the probability of a specific chain to react in any of the reactions of mechanism in Fig. 3 is a simple function of the chain mass and contour length (Supplementary Eqs. (13)–(16) and Supplementary Table 18). This allowed us to use just 12 independent kinetic parameters to define a realistic and tractable reaction network of tens of thousands of components (i.e., chains of unique size, composition and topology) that comprise a remodeling sample. These kinetic parameters reflect the weighted average kinetics of all chains in the sample. The excellent agreement between the observations and microkinetic simulations based on mechanism in Fig. 3 validates our coarse-graining strategy, which is independent of the underlying chemistry.

The importance of highly branched chains in determining the remodeling, revealed by our work, means that quantitative descriptions of remodeling must account for chain topology explicitly. This presents a particular challenge for mechanistic understanding and predictive simulations, because mixtures of branched chains are difficult to characterize experimentally11,62, while simulating the complex relationship between the size of a branched chain, its fragmentation probability, and the multitude of microstructures generated both by its fragmentation and by addition of the resulting macroradicals to random locations of other branched chains is resource-demanding. Analysis of mass-dependent distribution of small-molecule chromophores that are incorporated into chains either simultaneously or in competition with new bond formation offers useful mechanistic insights that simplify, accelerate or even reduce the need of full-scale simulations. For radical additions, pyrene-modified stable organic radicals, such as TEMPO, work well. For approaches reliant on small-molecule crosslinkers, incorporating a chromophore in the crosslinker will likely be similarly effective.

In conclusion, we described the molecular mechanism of spontaneous regeneration of backbone C–C bonds in mechanically-stressed polymer initiated by macroradicals products of scission of overstretched polymer chains. We demonstrate that even fairly inert unstabilized C–C bonds support the sufficiently facile formation of new bond for the average chain in the loaded sample to grow despite simultaneous competing chain scissions, providing means to suppress or even reverse mechanical degradation autonomously and in real time. Importantly for prospective practical applications of such constructive remodeling, it is compatible with O2 and commercial antioxidants, manifests clear and potentially exploitable dependence on the polymer composition, and requires neither mechanochemically-labile monomers, co-reactants nor complex chain architectures. The reported molecular mechanism enables detailed simulations of the evolving composition of the loaded material over usefully long loading times. Such simulations reproduced the experimental results accurately using relative rate constants similar to those calculated at the DFT level for model radicals. This confirms that the observed mechanochemistry reflects intrinsic kinetics and thermodynamics of the individual steps of the mechanism irrespectively of the specific means of generating the macro-radicals or the polymer studied. We also described a simplified method of predicting the competition between bond-forming and bond-breaking reactions without the need for extensive simulations. The presented approach and data provide a quantitative framework for systematic studies of polymers capable of forming new backbone bonds under load and of means to engineer this reactivity in practically relevant materials.

**Methods**

**Shearing experiments.** Polymer samples were sheared in a custom apparatus, comprised of a purpose-made capillary flow cell coupled to an 831.20 400 Hz Elastomer System from MTS Systems Corporation. This tester controls the magnitude and rate of the vertical displacement and measures the force needed to achieve them. The cylindrical flow cell consists of two reservoirs of 10 mm in diameter and 2.5 cm long (~2 mL capacity) each connected by a capillary of 1 mm diameter and 10 mm length (Supplementary Fig. 5) and two pistons fitting the reservoir chambers. During the operation, the two pistons were maintained at a constant vertical separation of 30 mm and the cell was moved up and down at a linear rate of 0.625 mm/s corresponding to a single shearing cycle of 32 s (the oscillation frequency of 0.0315 Hz). The temperature of the cell was maintained constant at 10 ± 2 °C using a cooling coil wrapped conformally around the cell distillation, for which a coolant was circulated while the temperature of the cell was monitored by a thermocouple inserted in a borehole orthogonal to the capillary. The cell was placed in a sealed glovebag to control the atmosphere around it and hence the gases dissolved in the sheared melt. The oxygen concentration in the bag was measured with a Setag oxygen analyser.

In each experiment, the flow cell was filled with the sample (1.4 g) in two steps. First, ~1.2 g of the copolymer was placed in one of the chambers as mm-size pieces, and the cell was subject to 4 shearing cycles, after which the cell was dismantled, and the remaining 0.2 g was added. For anaerobic shearing, all operations were performed under N2 atmosphere in the glovebag. Samples of sheared material of each sample were taken periodically from 3–5 different locations of the upper reservoir and stored under Ar at −37 °C until analysed. Variations of all measured parameters among samples taken from different locations of the reservoir were within the experimental uncertainties, suggesting homogeneity.

We confirmed that the sheared material equilibrates rapidly with the atmosphere around the cell during the experiment. For example, setting up the cell under N2 as described above with an N2-saturated copolymer sample and replacing the atmosphere surrounding the cell with air yielded the same mass-distribution and degree of peroxidation after >100 cycles as a similar sample that was loaded in the cell in air and the shearing was performed exclusively in air. Because the copolymer oxidizes spontaneously if slowly in air, its exposure to air before shearing should be minimised regardless of whether the sample is intended to be sheared in air or N2.

To estimate the contribution of local heating to remodeling of sheared samples, we sheared a 0.1% (mass) solution of anthracene dimer in the copolymer. The copolymer solution was a thermally labile species that undergoes thermal decomposition and forms anthracene upon mild heating (Supplementary Fig. 9). The characteristic absorption spectrum of anthracene enables its detection in sheared samples when >0.1% of the dimer dissociated during the shearing experiment. No detectable amount of anthracene was produced in sheared dimer-doped samples.

**Sample analysis.** THF solutions of sheared material for further analysis were prepared by adding a weighted portion of a sample (15 mg) to an aliquot of freshly distilled THF in a 1.5 mL vial, which was then shaken until the material dissolved. The sample was then transferred to a mini-centrifuge tube and centrifuged at 10,000 rpm (~6200 g in relative centrifugal force) to sediment any solids. For SEC analysis, a 100 µL aliquot of the supernatant was diluted with anhydrous THF to give ~0.5 mg/mL concentration (1.5 mg/mL for T-doped samples). The concentration of hydroperoxy moieties in hydroperoxy moieties in the sample was quantified by iodometry of iodometrically dissolved sheared material, by monitoring the absorbance of I3− formed in the reduction of hydroperoxy moieties. A 500 µL aliquot of a solution of a sheared sample was transferred to a spectral-glass cuvette, diluted with distilled THF (500 µL), anhydrous isopropanol (300 µL) and acetic acid (100 µL). All additions were performed under N2. After recording the absorption spectrum of the sample, a solution of NaI in isopropanol (15 mg in 100 µL) was injected into the sample, and the spectrum between 300–600 nm were collected every 36 s for 30 min (Supplementary Fig. 8).

Shearing of polymers containing dissolved pyrene-modified TEMPO, T, generates polymer chains bearing covalently bound T moieties when a C-based macroradical recombines with T. Pyrene served as a spectroscopic marker, thanks to its distinct UV–vis spectrum, to enable quantitation of polymer-bound TEMPO by UV–vis analysis of mass-resolved SEC fractions. We deconvoluted the spectrum at each retention time that manifested absorption at both 262 and 344 nm (which are absorption maxima for styrene and pyrene, respectively) of >3 mAU to the styrene and pyrene contributions using the reference spectra measured under the same conditions (Supplementary Fig. 15). Note that the [Tpoly]/[Tpyrene] ratios...
are independent of the chain mass and are therefore valid regardless of how the retention time and the chain mass are related. The total amount of polymer-bound T was quantified by deconvoluting the spectrum of the sample, rather than individual fractions.

**DFT calculations.** All computations were performed with the Gaussian 09.E software package at the (u)MPW1K/6-31+G(d,p) level. In addition we calculated six key activation enthalpies with 5 other functionals (Supplementary Table 3) to assess how sensitive the results were to the model chemistry.

To construct the minimum number of segments (chains of two or more repeat units terminated by CH₃ groups, Supplementary Fig. 18) that quantitatively capture the kinetics and stoichiometry of mechemanochemical fragmentation of a chain of styrene/butadiene copolymer of an arbitrary length and stretched to an arbitrary force at an arbitrary loading rate (because these parameters in sheared samples are unknown), we divided all backbone bonds of the styrene/butadiene copolymer into those formed during polymerisation (the “between” bonds) and those carried over from each monomer (the “within” bonds). To estimate the kinetics of mechemanochemical fragmentation of an arbitrary “between” bond of a stretched chain, we calculated force-dependent activation free energies of fragmentation of the “between” repeat unit segments to model macrochains.

In the absence of force homolysis of C=C bonds in these segments lacks transition states. To locate the transition states for mechemanochemical fracture of a C=C bond, we first optimized the longest conformer of each segment mentioned above with its C=C‚ ··· C=C distance constrained with a very soft virtual harmonic spring to the restoring force of 4.5 nN (implemented with the iop(1/164) overlay procedure of Gaussian). We then performed a relaxed potential energy scan (rPES) of the scissile bond in this externally constrained molecule, followed by Berry minimization of the scan point with the highest electronic energy to a (constrained) transition state.

The calculations of force-dependent activation energies followed the previously described method and experimentally validated method. First, we performed rPES on the longest conformer of each kinetically-significant stationary state by increasing its energetic content stepwise up to the restoring force of 6 nN. These scans yielded electronic energies and constrained distances at multiple increasingly large values of the stretching force. Second, we calculated analytically frequencies of a subset of the converged scan points to estimate force-dependent thermodynamic corrections. Such calculations are theoretically sound because they are performed on the molecule plus its infinitely-compliant constraint (rather than just the molecule), which is a stationary point with all internal forces at zero.

Finally, we interpolated electronic energies, distances and thermodynamic corrections to yield continuous ΔG and ΔH as a function of stretching force up to 6 nN (Supplementary Eq. (5)).

**Microkinetic mechanistic simulations.** We simulated the remodeling of the copolymer predicted by the mechanism in Fig. 3 by representing every chain by a specific chain sequence of unbonded inert repeat units (U, i.e. 10% of 2.5 kDa each repeating unit). The resulting mass-linkless chains each capable of linking an arbitrary number of U. All chemistry happens at a linker. The system is closed, of constant volume and spatially homogeneous, with no concentration gradients. The homogeneity of sheared samples was confirmed experimentally as described above. We ensured the finite size of the model without violating the conservation of mass by assuming that only chains whose concentration exceeds a threshold value react.

Fracture of a branched chain and addition of a macroradical to another chains create product chains of different topologies (see Supplementary Tables 16, 17 for examples). We manually defined the relationship between the distribution of product chain topologies for a specific chain topology. We then used this information to create product distributions programmatically (see the Supplementary Information for further details). We described each chain by a size vector, which is a sequence of integers in specific order that uniquely define the size of each chain segment and their relative position in the molecule, and related to the chain topology by systematic notation (Supplementary Table 15). A chain segment is a portion of a chain between two branch points or between a terminus and a branch point. Each number of the size vector is the number of U in each segment. A linear chain has a single segment and is coded by a single integer. An n-arm star chain is coded by a sequence of n integers in increasing order, each describing the size of each arm.

In sheared material a chain of each structure is present in several chemically significantly different for both pairs of homologues, validating our choice of two-dimensional MeC ordering that uniquely defines sequences in the data. We described each chain by a size vector, which is a sequence of integers in specific order that uniquely define the size of each chain segment and their relative position in the molecule, and related to the chain topology by systematic notation (Supplementary Table 15). A chain segment is a portion of a chain between two branch points or between a terminus and a branch point. Each number of the size vector is the number of U in each segment. A linear chain has a single segment and is coded by a single integer. An n-arm star chain is coded by a sequence of n integers in increasing order, each describing the size of each arm.
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Author contributions
M.C. and S.A. designed the instrument for shearing the copolymer and performed all shearing experiments. C.W. performed all analyses. C.W. and Y.T. carried out quantum-chemical calculations; Q.C., C.W., C.S. performed the simulations. M.C. and R.B. designed the project and supervised its execution. R.B. wrote the paper with input from M.C. and C.W.

Competing interests
The authors declare no competing interests.

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