

Editing of Polymer Backbones

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Abstract | Polymers are at the epicenter of modern technological progress and ensuing environmental pollution. Considerations of both polymer functionality and lifecycle are crucial in these contexts, and the polymer backbone—the core of a polymer—is at the root of these issues. Just as the meaning of a sentence can be altered through editing the words, so too could the function and sustainability of a polymer be transformed through chemical modification of its backbone. Yet, polymer modification has primarily been focused on the polymer periphery. In this Review, we attempt to bring a greater focus to transformations of the polymer backbone by defining some concepts fundamental to this topic (e.g., “polymer backbone” and “backbone editing”), collecting and categorizing examples of backbone editing scattered throughout a century’s-worth of chemistry literature, and outlining critical directions for further research. In so doing, we lay the foundation for the field of polymer backbone editing and hope to accelerate its development.

Introduction

The advent of synthetic polymers in the 20th century transformed global technology such that polymers are now an integral part of our daily lives. Living in the Polymers Age and confronted by the megaton scale of polymer production, humanity has begun to think more deeply about the lifecycle of these versatile materials. The dominant lifecycle paradigm consists of five phases: (1)

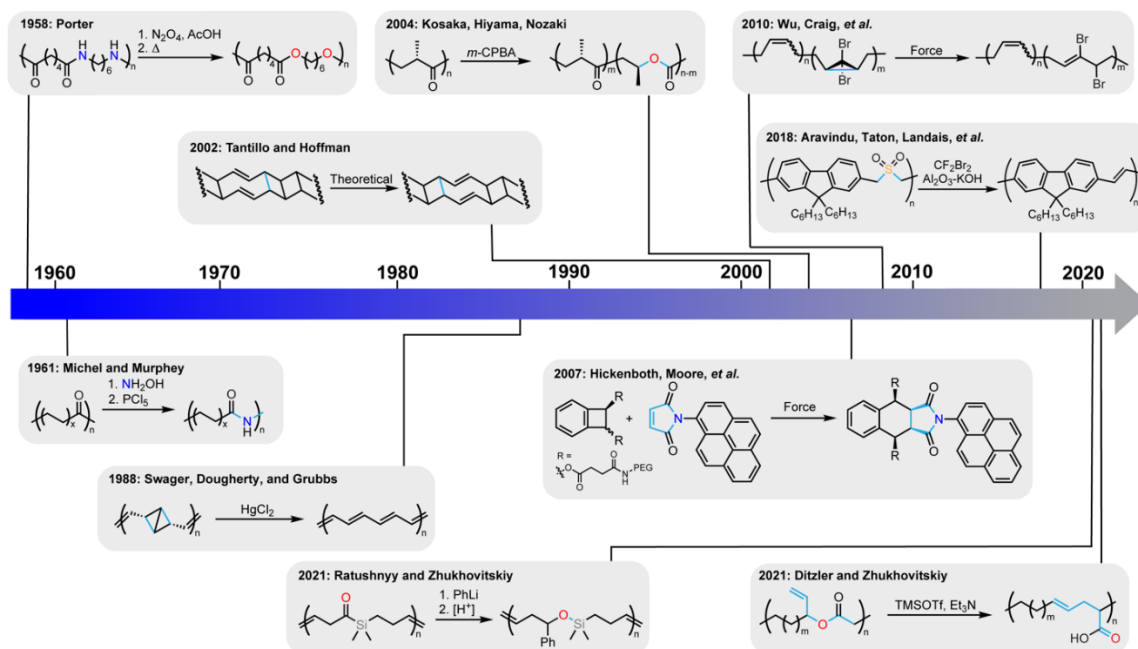


Figure 1 | A timeline of several major contributions to polymer backbone editing over the past 65 years, spanning the three classes of elementary edits: insertion/deletion,^{1–5} cyclization/de-cyclization,^{6,7} and rearrangement.^{8–10} Edited fragments are colored for emphasis.

synthesis/polymerization, (2) functionalization, (3) utilization, (4) re- or up-cycling, and (5) degradation/depolymerization. Once formed and up until the last phase of its lifecycle, the polymer backbone typically remains unchanged: a poly(olefin) remains a poly(olefin); a poly(ester)—a poly(ester). This fact often constrains our ability to build both function and features of sustainability into polymers; it also limits the scope of accessible polymeric materials. On the other hand, the ability to edit the composition of the polymer backbone offers a new phase of the polymer lifecycle, where it undergoes a metamorphosis of sorts, transforming from one class of polymers into another. This review begins by defining the concepts “polymer backbone” and its “editing,” then proceeds to describe the century-old history and state of the art in polymer backbone editing (Figure 1), and concludes by outlining exciting opportunities for further development of this nascent field. Transformations of the global topology of a polymer (e.g., linear to cyclic) and peripheral editing have been recently reviewed by others and will not be covered here.^{11–14}

Definitions

Polymer Backbone:

Before we can discuss skeletal editing of polymer backbones, we must discuss what we mean by “polymer backbone.” IUPAC defines a polymer backbone as “that linear chain to which all other chains, long or short or both, may be regarded as being pendant.”¹⁵ IUPAC also notes “where two or more chains could equally be considered to be the main chain, that one is selected which leads to the simplest representation of the molecule.”¹⁵ This IUPAC definition leaves considerable ambiguity between what is the backbone and what is the side chain. For example, whether hydrogen atoms of polyethylene are “backbone” or “side-chains” is unclear; similarly, if a ring is embedded or fused to a linear chain of atoms—e.g., in epoxidized 1,4-polybutadiene—are all the atoms of the ring considered to be part of the backbone? The situation becomes even more

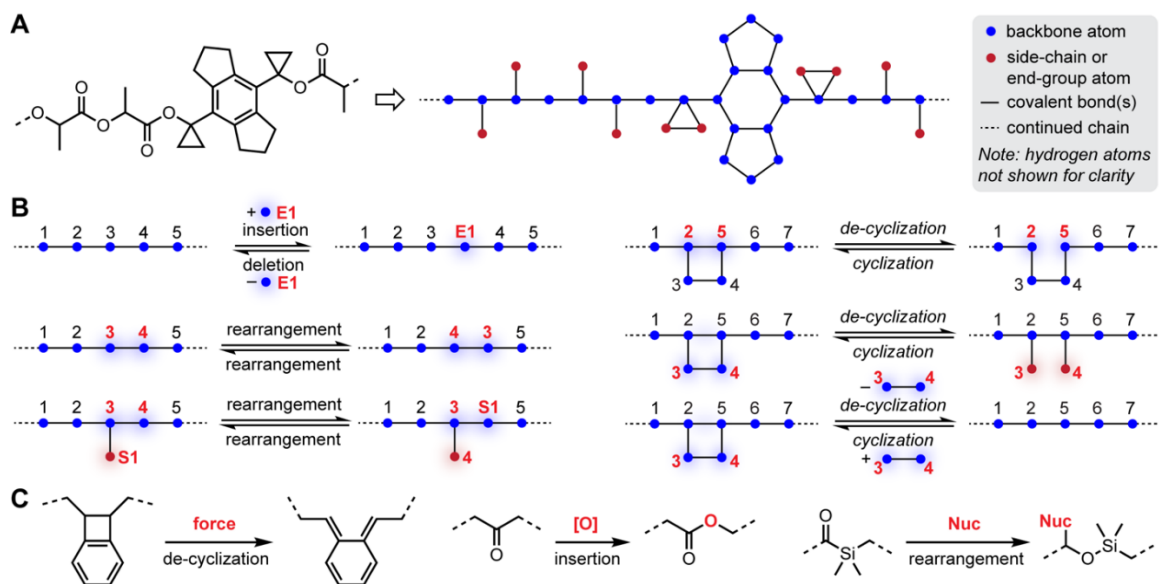


Figure 2 | **Defining polymer backbones and backbone editing through graph representation.** **A.** An example of a hypothetical polymer backbone and its graph representation, which shows which part is the backbone and which is sidechains or end-groups. **B.** Elementary backbone edits—insertion/deletion, cyclization/de-cyclization, and rearrangement—illustrated using graphs for a variety of scenarios. **C.** Representative reported examples of elementary polymer backbone edits, including force induced de-cyclization, Bayer-Villiger oxidation of a polyketone, and Brook rearrangement of a poly(acyl silane).

nebulous if we consider ladder-like, 2-dimensional, or more topologically complex polymers. The ambiguity in the definition of a backbone naturally leads to ambiguity in what is considered backbone editing, which could hamper the development of this field.

To address this issue, we propose a self-consistent definition of polymer backbones based on graph theory. To begin, we translate the polymer into a graph, where each atom is a vertex and each covalent bond is an edge, regardless of bond order or atom identity (Figure 2A). If the polymer has natural boundaries (e.g., end-groups in the case of linear polymer), we define as the backbone the set of all non-self-intersecting paths connecting these boundaries, excluding the boundaries themselves. In the case of polymers that lack boundaries (e.g., cyclic ones), we pick one vertex of the longest non-self-intersecting cyclic path in such a system to be both the beginning and end of the path. In this case, the artificial boundary vertex is included in the backbone. In the case of complex systems with multiple connected polymeric components, each such polymeric “branch” may be treated as an individual graph, with its own backbone.

Although this definition offers self-consistency and clarity—with the only exceptions being in the definition of end-groups and the subjective boundary between polymers and oligomers—the disregard for the actual geometry and chemistry of the polymer (e.g., *E/Z* isomer of a double bond, bond order, or identity of functional groups) may give rise to some situations that may be unnatural from a chemist’s perspective. We will discuss these situations in the next section focused on backbone editing, when the chemistry becomes relevant.

Polymer Backbone Editing:

While any chemical modification within the backbone of a polymer could in principle qualify as “editing,” we constrain the definition to changes that modify the corresponding polymer graph, excluding chain coupling/cleavage and chain extension/depolymerization (Figure 2B). An arbitrary backbone edit may be expressed as a single “edit” or combination of elementary “edits”: cyclization/de-cyclization, insertion/deletion of one or more atoms, and rearrangement of atoms (Figure 2B). Insertion refers to addition of atoms external to the *entire* polymer—i.e., not just backbone, but also end-groups and side-chains into the polymer backbone. Inversely, deletion refers to excision of backbone atoms such that they become external to the entire polymer. Meanwhile, rearrangements must include backbone atoms and may or may not include side-chain atoms—either way, all atoms inserted and/or moved must be polymer-bound. Thus, a substitution of one atom for another within the backbone of a polymer could be described as a combination of insertion and deletion; more complex combinations are also possible. Additionally, cyclization refers to the creation of a ring, such that this new ring is part of the polymer backbone; de-cyclization is the reverse of this process. Importantly, the nomenclature is a state function of the structure of starting and edited polymer backbone, independent of the mechanism.

Based on our definition, such transformations as hydrogenation of backbone alkenes would not qualify as backbone editing; on the other hand, Baeyer-Villiger oxidation of backbone carbonyl species would be described as an “insertion” edit (Figure 2C). As mentioned earlier, some transformations may technically fit our definition of backbone editing but may seem unnatural to consider this way. Although our definitions may leave some readers unsatisfied because of the “unnatural” situations, we hope that the benefits of clearer definitions outweigh these concerns.

Polymer Backbone Editing vs Skeletal Editing of Small Molecules:

Skeletal editing has a long history in the context of small molecules, and a recent review covered single atom logic as a reinvigorated subclass of such editing.¹⁶ Aside from the obvious difference—

small molecules versus polymers—one may wonder if there are fundamental differences in the chemistry of the transformations. The answer is yes, though the differences are subtle. Perhaps the biggest of these is the demand for exceedingly clean and high-yielding transformations in the context of polymers, which does not rise to the same level for small molecules. While products with editing errors can typically be separated from the target product in small molecule chemistry, the same will generally not work for polymers, whose backbone will preserve the record of multiple edits—both correct and erroneous. Furthermore, transformations that proceed via dissociative mechanisms (e.g., homolysis) might be effective in small molecule contexts, but may lead to undesired chain cleavage in polymers. More generally, polymer editing needs may require modifications of existing small molecule methods or development of new chemical transformations. Another issue is the effect of one edit on its neighboring edits—a point that is more pertinent in polymers than small molecules. Lastly, certain stimuli—e.g., tensile stress, generated by ultrasonication or macroscopic extension of a material (see *Force-induced Decyclization*)—may only be applicable to polymer chains. In short, although the two research directions have considerable overlap, they also have considerable distinctions that motivate their independent development.

Insertion

Insertion of Nitrogen:

The Schmidt rearrangement is a powerful method of effecting nitrogen atom insertion by converting aldehydes, ketones, or carboxylic acids to amides or amines by addition of azide salts under acidic conditions.¹⁷ In the context of polymers, the majority of Schmidt rearrangements have been reported to occur on side chains,^{18–22} however, several reports do exist of backbone Schmidt rearrangements of aliphatic and aromatic polyketones to polyamides (Figure 3A–B).^{1,23,24} The polyketones were either synthesized by copolymerization of CO and ethylene (aliphatic) or Friedel-Crafts reactions (aromatic), then subsequently treated with hydrazoic acid to yield the corresponding polyamides. Both Michel and Murphey and Takiguchi, Iwakura, and coworkers report > 84% for aromatic polyketones under traditional Schmidt conditions.^{1,23,24} In the presence of excess hydrazoic acid, Murphey and Michel also report 55% conversion of a polyamide to a polytetrazole;¹ however, the latter conversion is solely based on additional nitrogen incorporation as measured by elemental analysis.

Related to the Schmidt rearrangement is the Beckmann rearrangement: a two-step process that begins with oxime formation followed by Brønsted or Lewis acid-catalyzed rearrangement that results in formation of an amide group; the overall result is nitrogen insertion into the molecular skeleton. This transformation has also been demonstrated to convert polyketones to polyamides (Figure 3B).^{1,24} Murphey and Michel first report >90% conversion of the polyketone to a polyoxime based on elemental analysis. Subsequent conversion of the polyoxime to polyamide is mainly supported by IR analysis, since theoretical nitrogen incorporation doesn't change from oxime to amide.^{1,24} Takiguchi and coworkers observe similar results by IR, but also note considerable chain-scission for aromatic polyketones.¹⁹ For all these examples, it should be noted that elemental analysis and IR help confirm nitrogen insertion into the polymer, but these techniques weren't well equipped to distinguish between nitrogen containing products (e.g. amides and tetrazoles), identify and quantify side products, or quantify chain-scission. As such, these experiments ought to be replicated and subjected to modern polymer characterization techniques to unambiguously establish the product composition, structure, and molecular weight distribution.

Insertion of Oxygen:

benzocyclobutene, the mechanochemical pathway was found to always yield the *E,E*-isomer of the product. The mechanistic reason for this anomaly is that application of force to the *cis*-benzocyclobutene selectively reduces the barrier for the disrotatory electrocyclic ring-opening, enabling this thermally disallowed reaction.

More recently, our group reported anionic 1,2-Brook rearrangement of poly(acyl silane)s into poly(silyl ether)s, which was coupled with La(CN)₃-catalyzed benzoin cascade reactions to achieve backbone multi-atom insertion (Figure 3E).⁹ In this communication, both rearrangement and insertion backbone editing types are reported; discussion of the rearrangement is reserved for a later section, and only insertion editing will be discussed here. After synthesizing poly(acyl silane)s through acyclic diene metathesis polymerization (ADMET) and subjecting them to different classes of nucleophiles, Ratushnyy and Zhukhovitskiy used La(CN)₃-catalyzed Brook/benzoin cascade reactions to formally insert a “C–O” fragment.⁹ In addition to altering the polymer backbone, the Brook/benzoin cascade reaction introduces quaternary stereogenic centers and otherwise inaccessible pendent alkenes into the polymer without chain-scission. As may be expected, this editing transformed not only the polymer backbone, but also its thermal properties—specifically, the glass transition temperature of the polymer increased by as much as 30 °C.⁹

Atom insertion into polymer backbones is a powerful strategy to transform the molecular structure and properties of polymeric materials. Moving forward, the realization of possible applications—from polymer sustainability to delivery of therapeutic and diagnostic agents—calls for the development of new efficient insertion mechanisms and further optimization of existing ones. Ultimately, the chemistry invented out of this necessity is expected to prove valuable in the small molecule context as well, completing a positive feedback loop that will serve both fields well.

Deletion

To our knowledge, only one example of “deletion” polymer backbone editing has been reported to date. In 2018, Aravindu, Taton, Landais, and coworkers utilized the Ramberg-Bäcklund reaction to excise sulfur atoms in the form of SO₂ from poly(arylmethylene sulfone) backbones to convert them to poly(arylene vinylene)s and unveil useful optical properties characteristic of such conjugated polymers (Figure 3F).⁵ After purification, the edited polymers were isolated in low to moderate yields (43% and 53%) but, based on IR and NMR spectroscopy, the editing was essentially quantitative in these purified materials. Although other candidates for such processes exist in organic chemistry literature, undesired chain cleavage would inevitably accompany them.²³ Thus, the field of polymer backbone editing offers a challenge for synthetic chemists to develop other non-scissile (e.g., concerted) atom deletion transformations.

Cyclization

Cycloaddition:

Cyclization editing of polymer backbones has a century-long history, dating back to before the concept of a polymer was widely accepted. In 1922, Pummer and Burkhard first reported the epoxidation of natural rubber via the Prilezhaev reaction using stoichiometric peroxybenzoic acid.²⁷ The transformation produced “a tough rubber oxide insoluble in all solvents”—presumably, epoxide cross-linking took place under their reaction conditions.²⁷ Since this early pioneering work, numerous other reports appeared on the epoxidation of unsaturated polymers, including both highly efficient and selective transition metal-catalyzed and enzymatic methods.^{28–}

³³ Among these, the use of a topologically linked catalyst reported by Thordarson, Rowan, and

coworkers in 2003 is particularly remarkable because it suggests the feasibility of sequentially processive rather than random polymer modification (Figure 4A).³³

Besides epoxidation, a number of other cycloaddition type of cyclizations on polymer backbones have been reported. These transformations include cyclopropanation, as well as Paterno-Büchi, dipolar, Diels-Alder, and higher-order cycloadditions.^{34–46} The former is well-represented by (scorpionate)copper-catalyzed cyclopropanation of 1,4-*cis*-polybutadiene with ethyl diazoacetate, reported by Perez and coworkers to be quantitative and lead to a 106 °C increase in the polymer's T_g .^{47–52} As another set of examples, Cetin, Durmaz, and coworkers published a thorough study of 1,3-dipolar and Diels-Alder cycloadditions on polyesters with backbone-embedded acetylene dicarboxylate moieties (Figure 4B).⁵³ They evaluated numerous dipoles and dienes—azide, oxime, nitron, furan, 2,3-dimethyl-1,3-butadiene, and anthracene—and observed nearly complete conversions (80–100%) within 16 hours at 40 °C for the dipolar cycloadditions, and ~80% conversion after 16 hour at 80–120 °C for the Diels-Alder ones.⁵³ Taking advantage of the disparate temperature regimes, the authors were able to execute sequential dipolar and Diels-Alder backbone cycloadditions on the same polymer backbone. Lastly, the authors explored further reactivity of the oxanorbornadienes obtained via the polymer/furan Diels-Alder reaction.⁵³ Addition of benzyl azide led to effective backbone substitution⁵³ and will therefore be discussed in the “Combination of Different Elementary Edits” section further down. Similarly, recently reported inverse-demand cycloaddition at the polymer backbone also leads to effective backbone substitution and will be discussed later.⁵⁴

Side-chain cyclization:

Cyclization through intramolecular linking of side-chains has been thoroughly studied for a wide range of polymers. Perhaps the earliest report of such a process is from Herrmann and Haehnel, who studied poly(vinyl alcohol) and found that it successfully forms acetals with benzaldehyde in the late 1920s.⁵⁵ Poly(vinyl acetal)s—especially poly(vinyl butyral)—have since then become a valuable industrial material, with numerous applications including coatings and adhesives⁵⁶; development of novel poly(vinyl acetal)s—e.g., more sustainable ones—continues to be a subject of modern research.^{57,58}

Other condensation-type mechanisms—e.g., aldol condensation, lactonization, and anhydride formation—have been explored in the subsequent years.^{59–68} A seminal example of these studies is the 1960 report by Grant and Grassie on the thermal dehydration of poly(methacrylic acid): using IR spectroscopy, they determined that the predominant product was the formation of six-membered cyclic anhydrides along the polymer backbone.⁶⁹ Since then, analogous dehydration of poly(carboxylic acid)s and related lactonizations and ketalizations have been elucidated^{70–72} and, more recently, utilized to derive function. The latter is exemplified by the 2012 report by Bates, Willson, and coworkers, in which poly(maleate)-based films are subjected to thermal cyclization to switch their polarity and enable challenging block-copolymer feature alignment (Figure 4C).⁷³

Alternative mechanisms have also been explored in this context; a notable example is olefin metathesis. Metal alkylidene catalyzed ($M = Ru$ or Mo) ring-closing metathesis of 1,2-poly(*Z*-pentadiene) or poly(epoxybutene) yields polymer backbones with 5- and 6-membered rings, respectively (Figure 6A).^{74,75} In both cases, some larger cycles are formed at early reaction times when non-adjacent olefins undergo ring-closing metathesis (RCM); however, since both ring-closing and ring-opening metathesis are active under the reaction conditions, if larger rings were formed initially, the system is able to “correct previous errors” and eventually reach the thermo-

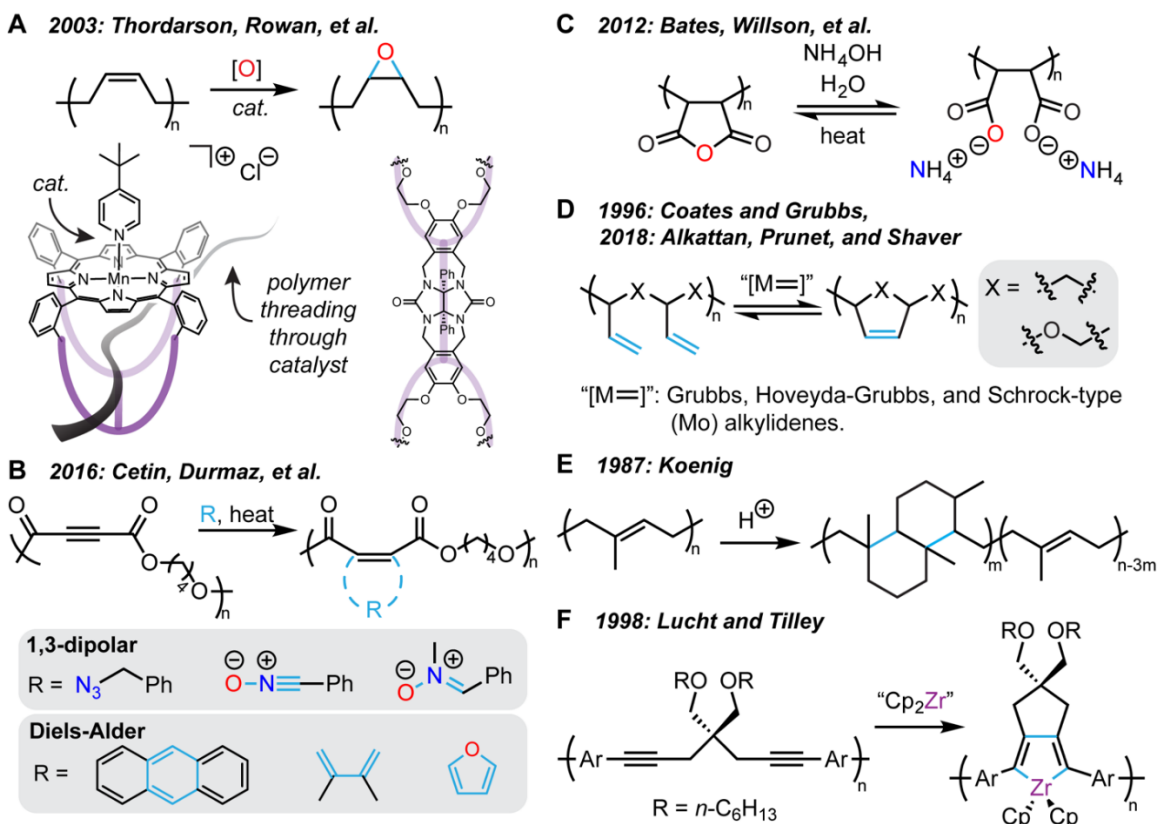


Figure 4| **Cycloaddition (A, B), side-chain cyclization (C, D), and multi-cyclization (E, F) of polymer backbones as a mode of polymer backbone editing (color is used to emphasize edits).** **A.** Epoxidation of unsaturated 1,3-poly(butadiene) with a topologically linked catalyst.³³ **B.** 1,3-dipolar and Diels-Alder cycloadditions to polyesters containing acetylene dicarboxylate moieties.⁵³ **C.** Polymer backbones containing maleic anhydrides which ring-open or ring-close in the presence of base or heat respectively.⁷³ **D.** Metal alkylidene catalyzed ring-closing metathesis of poly(pentadiene) and poly(epoxybutene) to form 5- and 6-membered rings in the polymer backbones.^{74,75} **E.** Cyclization of natural rubber where at most three consecutive alkenes cyclize in the polymer backbone.⁷⁶ **F.** Multicyclization via zirconocene coupling of main-chain alkynes.⁷⁷

dynamic minimum with > 97% conversion to the 5-membered rings and > 99% conversion to the 6-membered rings.^{74,75}

Lastly, side-chain cyclization also underpins “peptide stapling” and single-chain polymer nanoparticle (SCNP) formation inspired by the fold-stabilizing function of disulfide bridges naturally present in numerous proteins.⁷⁸ Peptide stapling and SCNP synthesis methods include a broad range of mechanisms, which have been reviewed elsewhere.^{78–81} We direct the interested readers to these reviews for more detail.

Miscellaneous (multi-)cyclization:

Though not exhaustive, this section aims to highlight a few key miscellaneous examples of cyclization backbone editing processes. A number of diene polymers—natural rubber,^{76,82,83} poly(isoprene),^{84–87} poly(butadiene),^{88–91} and various derivatives^{92–96}—have been subjected to backbone cyclizations that proceed via carbocation intermediates (Figure 4E). These cyclization events occasionally link >2 repeat units (i.e., multi-cyclizations) and form ladder-like polymers in a process reminiscent of steroid biosynthesis.⁹⁷ In a related example, Kamigaito and coworkers

demonstrated that a styrene-diene copolymer undergoes acid-catalyzed Friedel-Crafts alkylation of side-chain benzenes with backbone carbocations.⁹⁸ Notably, Friedel-Crafts reactivity featured greater control of the polymer cyclization compared to the typical cationic conditions. Recently, Swager and coworkers applied a similar approach to transform triptycene-based polymers with pendent alkynes into a rigid ladder-like polymer.⁹⁹ Complementary to the Friedel-Crafts is the recent report by Shida, Inagi, and coworkers of nucleophilic aromatic substitution of fluoride with pyridine to form rod-like polymers with fused rings.¹⁰⁰ Organometallic chemistry has also been utilized to (multi-)cyclize backbone fragments, as exemplified by the 1998 report by Lucht and Tilley of zirconocene coupling of backbone-embedded alkynes into zirconacyclopentadienes (Figure 4F).⁷⁷ Lastly, some reports of mechanochemical de-cyclization discussed in the section below have also been accompanied by thermal—typically, electrocyclic—cyclizations.^{2,101,102} Thus, a wide assortment of methods is available to the polymer chemist for the post-polymerization installation of backbone rings.

De-Cyclization

Chemically- and Thermally-induced De-cyclization:

Many of the cyclization reports cited above—e.g., Diels-Alder cycloaddition, lactonization, anhydride formation, and olefin metathesis—also describe the reverse—i.e., de-cyclization—process. Though some of the force-induced de-cyclizations discussed below will harken back to these reports, this section will instead overview seminal examples of irreversible de-cyclizations. Among the earliest examples of the latter is the vulcanization of epoxidized 1,3-poly(butadiene) with multi-functional cross-linkers like dicarboxylic acids and polyamines, which proceeds through the nucleophilic ring-opening (Figure 5A).^{103,104} Analogous transformations have been explored

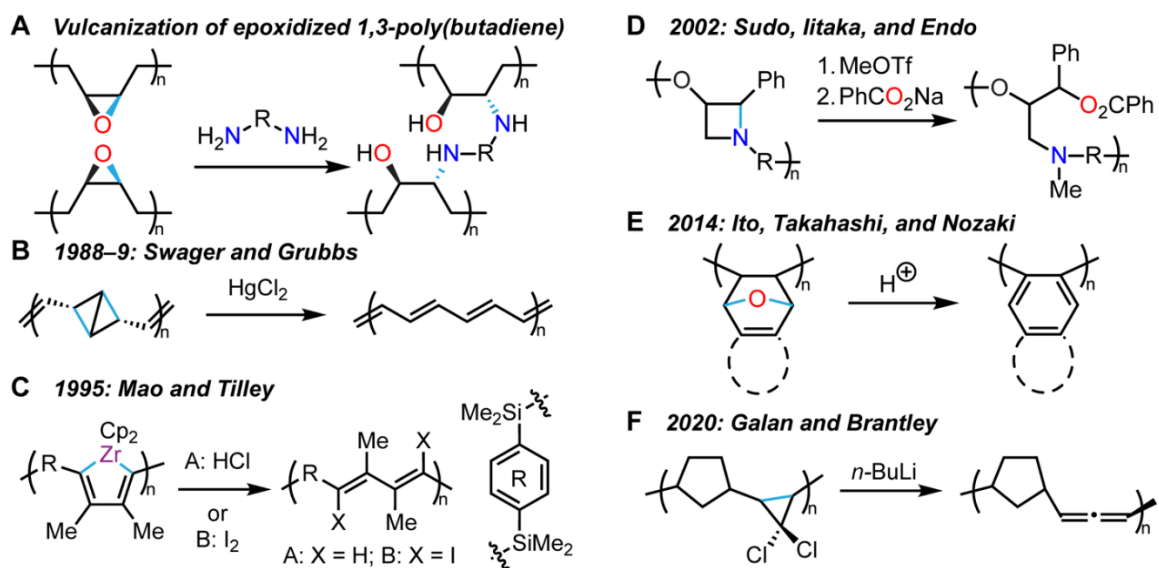


Figure 5 | **Chemically and thermally induced de-cyclization of polymer backbones on multiple substrates (color is used to emphasize edits).** **A.** Epoxidized 1,3-poly(butadiene) was reported to have undergone vulcanization with polyamines via nucleophilic ring-opening.^{103,104} **B.** Ring-opening of poly(benzvalene) by Swager and Grubbs in 1988–9 with HgCl_2 to form highly electrically conductive poly(acetylene).^{6,105,106} **C.** Proto- and iodo-dezirconation of zirconocyclopentadiene fragments in polymer backbones developed by Tilley and Mao.¹⁰⁷ **D.** Ring-opening of polymers containing azetidines by sequential treatment with methyl triflate and sodium benzoate.¹⁰⁸ **E.** Synthesis of poly(*o*-arylene)s by acid-promoted de-cyclization of poly(oxabicyclic alkenes).⁷¹ **F.** Skattebøl rearrangement of poly(dichlorocyclopropane)s induced by lithium-halogen exchange.¹⁰⁹

over the years for other unsaturated polymers like poly(norbornene).¹¹⁰

Other strained or otherwise reactive ring systems have also been coopted for de-cyclization backbone editing. For instance, in the late 1980s, Grubbs and Swager transformed insulating poly(benzvalene) into electrically conducting poly(acetylene) through treatment with HgCl₂ and subsequent doping with iodine (Figure 5B).^{6,105,106} Beautiful examples of polymer backbone de-cyclization of reactive metallacyclopentadienes to produce 1,3-diene segments in the polymer backbone have also been reported by Tilley^{77,107,111–113} (zirconium) and, more recently, by Tomita^{114–117} (titanium) (Figure 5C); Tomita also demonstrated related lithium-tellurium exchange to de-cyclize tellurophenes in polymer backbones.¹¹⁸ The metallocyclopentadiene chemistry has, in fact proven quite efficient and versatile, offering numerous more complex backbone editing opportunities (*vide infra*). Another notable example is a ring-opening of backbone azetidines, which Sudo, Itaka, and Endo accomplished by activation with methyl triflate followed by nucleophilic attack with sodium benzoate (Figure 5D).¹⁰⁸ In 2014, Nozaki and coworkers reported dehydrative de-cyclization of [2.2.1]-oxabicycles in polymer backbones which converts the polymers into poly(arylene)s (Figure 5E).⁷¹ More recently, Brantley and Galan utilized the lithium-halogen exchange-induced Skattebøl electrocyclic ring-opening to transform poly(dichlorocyclopropane)s into poly(allene)s (Figure 5F).¹⁰⁹

Force-induced De-cyclization:

Electrocyclic ring-openings also happen to be the first reported force-induced ring-opening (FIRO) processes. In their seminal 2007 reports, Potisek, Hickenboth, Moore, and their coworkers demonstrated that benzocyclobutenes embedded in polymer backbones undergo 4 π -electrocyclic ring-opening, when the polymer chains are subjected to adequate force through ultrasonication (Figure 3D).^{2,25} The ring-opened species—*o*-quinone dimethide—is not observed directly, but instead trapped by cycloaddition, the net result of which is multi-atom insertion, which we already described in the insertion section above.^{2,25} In their paper, Potisek, Moore, and coworkers also pioneered FIRO of spiropyran, which undergo 6 π -electrocyclic ring-opening into a merocyanine form with a concomitant change in color; notably, in the absence of force, the merocyanine can revert to the ring-closed spiropyran form (Figure 6A). Davis, Sottos, and coworkers extended the application of spiropyran to visualize stress in elastomers subjected to extension or compression.¹⁰¹

Building on these pioneering studies, more sophisticated force-responsive moieties—i.e. mechanophores—that undergo FIRO have been developed. Other color-changing mechanophores have been studied by Boulatov, Craig, and Robb groups.^{119–124} Craig and coworkers developed alternative mechanophores—e.g., ones based on *gem*-dihalocyclopropanes (Figure 6B)—and pioneered the use of single-molecule force spectroscopy (SMFS) to measure the forces needed to enable FIRO.^{7,125–133} Aside from electrocyclic and cyclopropane ring-openings, FIRO has also encompassed cycloelimination reactions described in studies published by Moore,¹³⁴ Craig,^{135–139} Boydston,^{140,141} Boulatov,⁵³ Xia,^{142–144} Wang,¹⁴⁵ and others.¹⁴⁶ In these transformations, a strained fused ring within a polymer backbone cleaves under applied force to either release stored length (case A) or eliminate a portion of the fused ring (case B). A particularly elegant example of case A was reported by Martinez, Burns, and Xia, who converted insulating poly(ladderane) into conducting poly(acetylene) through sonication (Figure 6B).¹⁴² To demonstrate case B, Larsen and Boydston utilized oxanorbornadiene (OND) mechanophores.^{140,141} Upon mechanical compression of a polymer network with embedded ONDs, a retro-Diels-Alder reaction occurs which eliminates the furan portion of the OND, leaving behind an alkyne embedded within the polymer backbone (Figure 6C).^{140,141}

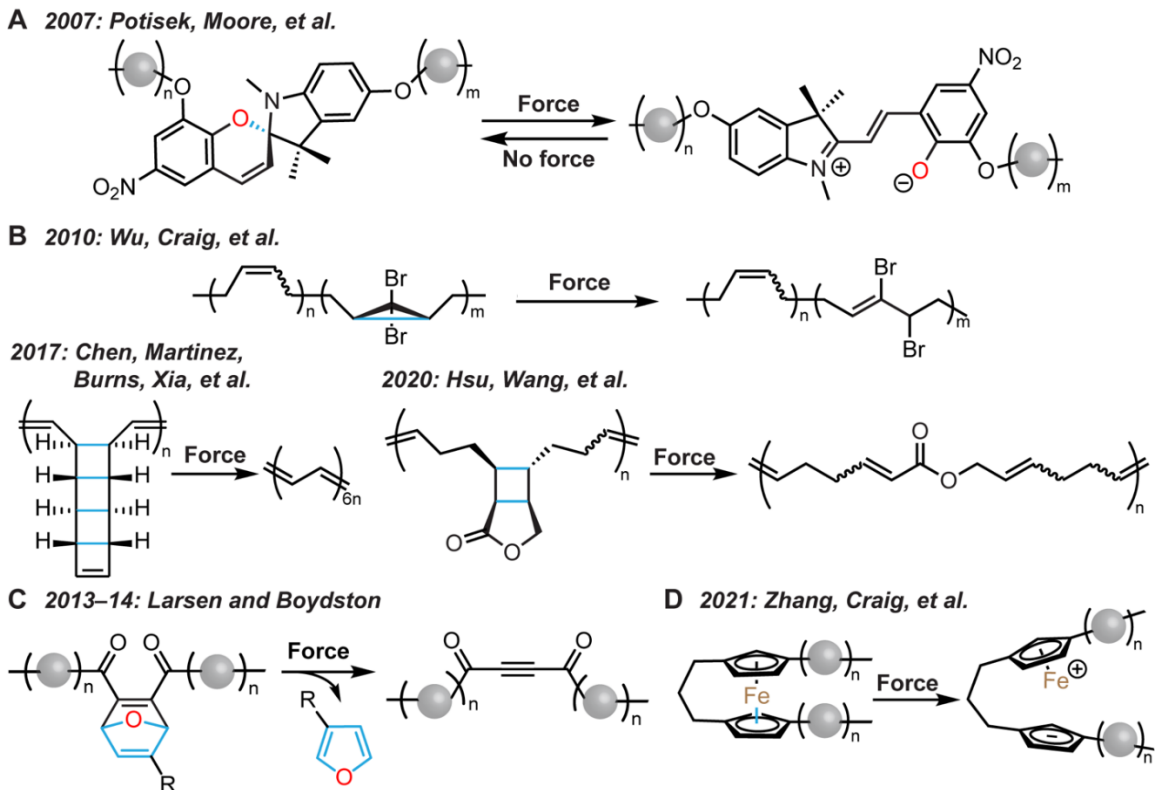


Figure 6 | **Force-induced de-cyclization of mechanophores embedded into polymer backbones (color is used to emphasize edits).** **A.** Illustration of FIRO via electrocyclic ring-opening of spiropyran embedded into a polymer backbone, resulting in stress responsive materials which indicate regions of stress through color changes.^{2,25} **B.** FIRO via electrocyclic ring-opening of *gem*-dibromocyclopropanes by Wu, Craig, and coworkers where mechanophores are present through the entire backbone.⁷ Release of stored length by FIRO of a fused cyclobutene and lactone system resulting in a degradable polymer backbone.¹⁴⁵ FIRO of polyadderane to polyacetylene via cycloelimination by Xia and Burns and coworkers, facilitating release of stored length.¹⁴² **C.** Retro-Diels-Alder de-cyclization through force in polymer networks containing embedded oxanorbornadiene moieties.^{140,141} **D.** Force-induced dissociation of Fe from Cp rings in the polymer backbone.¹⁴⁷

Similarly, Gossweiler, Craig, and coworkers demonstrated cycloelimination of a triazolinedione-anthracene adduct. Due to the stability of the cycloadduct, FIRO was only observed at temperatures above 125 °C.¹⁴⁸ Lastly, in what is best characterized as a combination of cases A and B, Zhang, Craig, and coworkers demonstrated FIRO of polymer backbone-embedded *ansa*-ferrocenes, which both released stored length and induced dissociation of Fe²⁺ from the cyclic sandwich complex (Figure 6D).¹⁴⁷

From the discussion above, we conclude that de-cyclization editing has received considerable attention over the years. Yet, most of the examples are either reversible or rely on organometallic reactivity, intrinsic ring-strain, and/or extrinsic tension to enable these transformations. For instance, photo-mediated de-cyclization of polymer backbones has scarcely been explored to date.^{149,150} Consequently, the scope of polymer backbones that can be edited this way remains limited. Nonetheless, even this limited scope convincingly demonstrates the power of de-cyclization to transform the properties of materials and serves as a foundational pillar of the growing field of mechanochemistry.

Rearrangements of Polymer Backbones

Associative Exchange:

Associative exchange reactions comprise some of the most thoroughly studied types of polymer backbone rearrangements. Among them, acyl transfer is perhaps the most widely practiced: from ligations utilized in polypeptide synthesis¹⁵¹ to network strand reorganization in vitrimers.^{152,153} For instance, since the first report of native chemical ligation,¹⁵⁴ which features S-to-N acyl transfer, it has been used for the synthesis of over 700 proteins as well as to link synthetic polymer chains.^{151,155–158} Note that although we do not consider chain coupling “backbone editing,” the isolated acyl transfer step technically is. A clearer case of such a rearrangement edit was reported in 2016 by Suzuki and coworkers: they prepared a polythioester with a protected pendent amine, whose deprotection induced S-to-N acyl transfer along the polythioester backbone, in the process transforming it into a polyamide.¹⁵⁹ Though this transformation appears to be nearly quantitative, it was also likely accompanied by cross-linking, as evidenced by model reactions. Analogous N-to-O acyl transfers in hydroxyl-containing polypeptides have been established since 1960 to proceed reversibly under acidic conditions.^{160,161} More recently, the reverse process—O-to-N transfer—was coopted by Tailhades, Martinez, Amblard, and coworkers in to transform polyesters into polyamides (Figure 7A).¹⁶² This transformation was complete with 1 hour at room temperature in both organic (*N,N*-dimethylformamide/triethylamine) and aqueous (phosphate buffer at pH = 7.4) media.¹⁶² The solubility of the resulting polyamides contrasted that of the starting polyesters: the latter were poorly soluble in the organic media but dissolved readily in the aqueous buffer; the former aggregated into beta-sheets and precipitated in the aqueous buffer but dissolved into the organic media.¹⁶² Building on this work, numerous other examples of polymer backbone editing via O-to-N acyl transfer have been reported by multiple groups in the last decade.^{163–167}

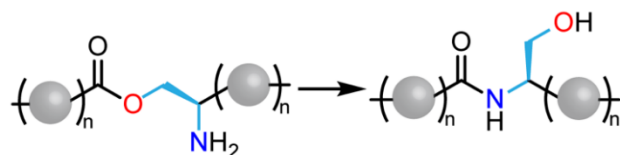
Meanwhile, in 2011, Montarnal, Leibler, and coworkers introduced the concept of a “vitriimer”—a thermoset that can undergo associative exchange reactions among the network strands.¹⁶⁸ In this seminal work, the authors demonstrated the ability of a hydroxy-ester network to undergo backbone/side-chain transesterification reactions, which enabled the thermoset material to be heat-processable, unlike conventional thermosets (Figure 7B).¹⁶⁸ During the last decade, vitriimer design has rapidly expanded to include a variety of polymers (e.g., polyesters, polybutadiene, and polyhydroxyurethanes) and rearrangement mechanisms.^{152,153}

Sigmatropic Rearrangements:

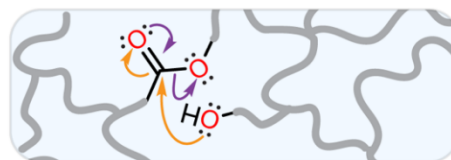
Sigmatropic rearrangements¹⁶⁹ have also been explored, albeit less extensively, in the context of polymer backbone editing, beginning with the theoretical studies by Tantillo and Hoffmann in 2002.^{8,170} The focus of Tantillo and Hoffmann’s work was on hypothetical polymers they called “sigmatropic shiftamers,” in which a structural defect (e.g., a σ -bond “surrounded” by π -bonds) can propagate along the polymer through successive sigmatropic rearrangements.¹⁷¹ There are four main types of shiftamer structures studied throughout their work: (1) ladderane shiftamers,⁸ (2) σ -polyacene,¹⁷² (3) helicoid [1,7]-shiftamers,¹⁷⁰ and (4) tape [1,5]-shiftamers.^{171,173} The latter two shiftamer types are technically not examples of backbone editing as we define it because the backbone graph remains unchanged; thus we will not discuss them further.

The first theoretical study of sigmatropic shiftamers by Tantillo and Hoffman explored the Cope rearrangement within [∞]-ladderane—an infinite molecule made of fused cyclobutanes—in which the internal σ - and π -bonds can migrate down the entire backbone (Figure 7C).^{8,171} Fluxionality of the system at room temperature was predicted because the calculated energy barrier of rearrangement was approximately 15 kcal/mol.⁸ Another type of shiftamer envisioned

A 2011: Tailhades, Martinez, Amblard, et al.



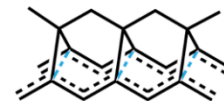
B 2011: Montarnal, Leibler, et al.



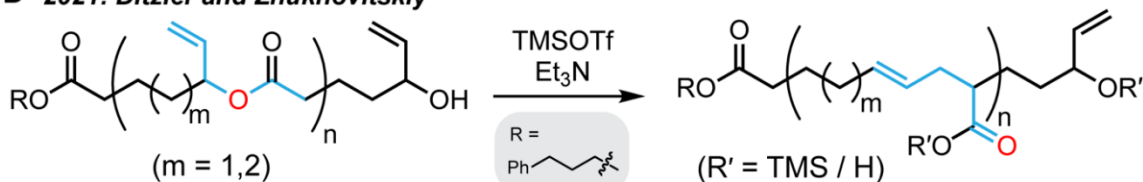
C 2002: Tantillo and Hoffmann



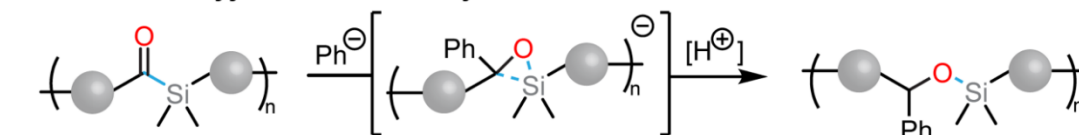
2004: Tantillo and Hoffmann



D 2021: Ditzler and Zhukhovitskiy



E 2021: Ratushnyy and Zhukhovitskiy



2021: Huang, Toste, et al.



F 1994: Tomita, Nishio, and Endo

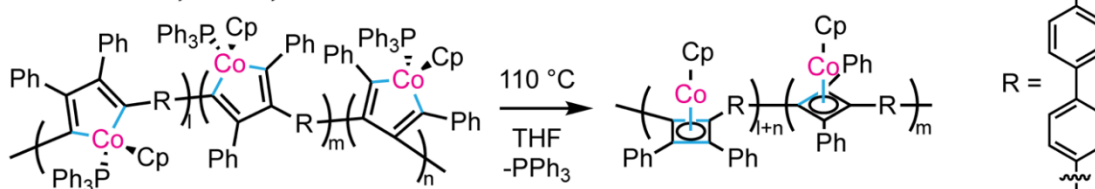


Figure 7 | **Rearrangements of polymer backbones (color is used to emphasize edits).** **A.** O-to-N acyl transfer to transform polyester to polyamide backbones.^{159,162} **B.** Associative acyl transfer in vitrimers of pendant alcohol chains with backbone ester moieties by transesterification.^{152,153,168} **C.** Theoretical sigmatropic rearrangements of a class of hypothetical polymers called “sigmatropic shiftamers” by Tantillo and Hoffmann. Ladderane shiftamers undergo Cope rearrangements allowing π -fragment migration down the shiftamer “backbone”.^{8,171} σ -Polyacenes in which σ -bond migration occurs along tethered polyene chains.^{171,172} **D.** Ireland-Claisen rearrangement of polyesters to form vinyl polymers in one step allowing for increased glass transition temperature and thermal stability.¹⁰ **E.** Brook rearrangement of poly(acyl silane)s reported simultaneously by Zhukhovitskiy and Toste for formation of poly(silyl ethers) and polymer backbone degradation respectively.^{9,174} **F.** Reductive elimination of cobaltocyclopentadiene to form (η -4-cyclobutadiene)cobalt fragments embedded in the polymer backbone.¹⁷⁵

by Tantillo and Hoffmann—a σ -polyacene—features σ -bond migration along a pair of polyene chains tethered to one another with short organic bridges (Figure 7C).^{171,172} These systems were predicted to in fact form delocalized bonds along the length of the polymer. Though the sigmatropic shiftamers envisioned by Tantillo and Hoffmann have not yet been realized

experimentally, they demonstrated the untapped potential of sigmatropic rearrangements to unlock unusual properties in the context of polymers.

Experimentally, sigmatropic rearrangements have begun to be realized in polymers in the last decade. However, these early examples constituted side-chain modifications—e.g., the Johnson-Claisen rearrangement of graphene oxide.¹⁷⁶ More recent examples of diaza-Cope rearrangement/polymerization, reported by Choi and Hwang in 2021 and Doyle-Kirmse reaction/polymerization of bis(allyl sulfide)s and bis(α -diazoester)s reported by Wang in 2022, are ambiguous by our definition because the rearrangements take place as the polymer backbone is forming rather than after the fact.^{177,178}

Around the same time, our group provided an unambiguous example of polymer backbone editing via sigmatropic rearrangements. Namely, Ditzler and Zhukhovitskiy reported that Ireland-Claisen rearrangements (ICRs) can transform poly(ester)s into vinyl polymers. Highly efficient ICR of polyesters containing pendent vinyl groups to resulting vinyl polymers was induced through addition of triethylamine and trimethylsilyl triflate resulting in clean reactivity, no chain cleavage, and conversions above 88% (Figure 7D).¹⁰ Meanwhile, the glass transition temperature (T_g) increased by as much as 61 °C and the thermal stability, assessed by thermogravimetric analysis, increased by as much as ~95 °C.¹⁰ Notably, one of the products of backbone ICR was equivalent to perfectly alternating poly(1,4-butadiene-*co*-acrylic acid) which is difficult to synthesize with the same chain microstructure/*co*-monomer alternation through conventional radical polymerization methods. Another vinyl polymer product had an unprecedented backbone composition.

Miscellaneous rearrangements:

Another rearrangement of polymer backbones closely related to sigmatropic ones was independently reported in 2021 by the groups of Zhukhovitskiy and Toste: anionic and photochemical (respectively) 1,2-Brook rearrangements of poly(acyl silane)s into poly(silyl ether)s. In the Zhukhovitskiy report, treatment of poly(acyl silane) with phenyl lithium transformed a poly(acyl silane) into a poly(silyl ether) in nearly quantitative manner (Figure 7E).⁹ Critically, the polymer chains remained intact, and a noticeable change in glass transition temperature (T_g) from -43 °C for the poly(acyl silane) to -12 °C for the poly(silyl ether) was observed.⁹ In the Toste report, irradiation of the poly(acyl silane)s with 390 nm UV lamp in wet chloroform led to substantial polymer degradation due to hydrolysis of the intermediate carbene, as showcased by GPC analysis (Figure 7E).¹⁷⁴ Degradation of the poly(acyl silane) was also affected in solid state and resulted in 28% mass loss after UV irradiation and sonication of studied copolymer.¹⁷⁴

Metallocyclopentadiene moieties in polymer backbones also offer opportunities for unique backbone rearrangements. Namely, heating cobaltcyclopentadiene-containing polymers at 110 °C in tetrahydrofuran leads to quantitative reductive elimination, which generates (η^4 -cyclobutadiene)cobalt fragments, where the cyclobutadienes are embedded in the polymer backbone (Figure 7F).¹⁷⁵ The polymers produced by this remarkable reaction have similar molecular weight to the starting polymer, suggesting that no chain cleavage took place.¹⁷⁵ Lastly, the material's color changes from brown to yellow during the course of the rearrangement, and the resulting polymer is highly thermally stable: 5% mass loss was observed at 482 °C!¹⁷⁵

The examples above demonstrate the power of backbone rearrangements to enable both new retrosynthetic strategies toward desired polymer backbones and new ways to alter material properties on demand.¹⁷⁹ However, the currently reported polymer backbone rearrangements

are only a small fraction of possible rearrangements that could be explored, given the plethora of reported small molecule rearrangements and the vast number of polymer chemical compositions.

Combinations of Different Elementary Edits

All the aforementioned examples of editing consist of a single elementary step; however, some edits are best thought of as a combination of elementary steps. For example, substitution of a backbone atom for another atom that originates outside of the polymer structure is a combination of deletion and insertion. In theory, any elementary steps could be combined, but the simplest combinations consist of non-degenerate pairings of an edit and its corresponding reverse edit (e.g. insertion/deletion and cyclization/de-cyclization). One such example is the conversion of a polyamide to a polyester via thermal decomposition of a poly(nitroso-amide), which represents a combination of nitrogen deletion and oxygen insertion edits (Figure 8A).⁴ In the reported transformation, nylon 6,6 yarn was nitrosated using a mixture of nitrogen tetroxide, acetic acid, and sodium acetate, and then heated to induce the backbone transformation (Figure 8A). At temperatures <100 °C, >95% conversion to the poly(ester) was determined by IR and elemental analysis of the products; however the polymer molecular weight was estimated to drop precipitously due to chain-scission: from 10,000–12,000 g/mol to 300–500 g/mol.⁴ The resulting poly(ester) yarns had several differences in properties compared to their poly(amide) counterparts. As the percent of ester incorporation increases, the moisture retention decreases, which we speculate is due to the increased hydrophobicity of the poly(ester) compared to the poly(amide). Meanwhile, the increase in the coefficient of friction and decrease in modulus were both attributed to chain-scission during the transformation, which created a rough surface with broken strands.

Beginning in 1995,¹⁸⁰ a wide variety of insertion/deletion edit combinations have been demonstrated for metallocyclopentadiene-containing polymer backbones. Tomita, Endo, and coworkers studied the cobalt system discussed in the rearrangements section and discovered that they could delete the cobalt and insert isocyanates, sulfur, and nitriles to generate pyridones, thiophenes, and pyridines, respectively.^{180–182} These transformations required heating above 110 °C, which led to competitive rearrangement (*vide supra*), rendering the insertion/deletion edit less than quantitative (e.g., ~68% conversion to pyridones).¹⁸⁰ Meanwhile, Tilley and coworkers conducted similar studies on zirconocyclopentadiene-containing polymer backbones and observed that these moieties could be converted at room temperature to substituted benzenes, thiophenes, thiophene oxides, and phospholes (Figure 8B).^{111,112,183,184} Notably, these reactions could be carried out at room temperature, and isolated polymers suggested quantitative functional group conversion, though the isolated yields were not always high: the authors noted that insoluble gel side-products were also frequently observed in these reactions, possibly due to polymer aggregation. More recently, analogous chemistry of titanocyclopentadienes has been developed by Tomita and coworkers, extending the scope of heterocycle products to selenophenes, arsoles, and stannoles.^{114,116,185–188} Like with zirconium, the titanium chemistry proceeded at or below room temperature, though it typically required ambient light as well; also the edited polymers were typically isolated in sub-90% yields—sometimes as low as 50%—though the reason for these imperfect yields was not discussed in detail.

Other combinations of insertion and deletion are the aforementioned examples of reactions between oxanorbornadiene containing polymers with benzyl azide⁵³ (Figure 8C) and inverse-demand cycloaddition (IDC) of tetrazines and trans-cyclooctenes (Figure 8D).⁵⁴ In each case, there is a cycloaddition, which results in insertion, followed by elimination of a small molecule, which

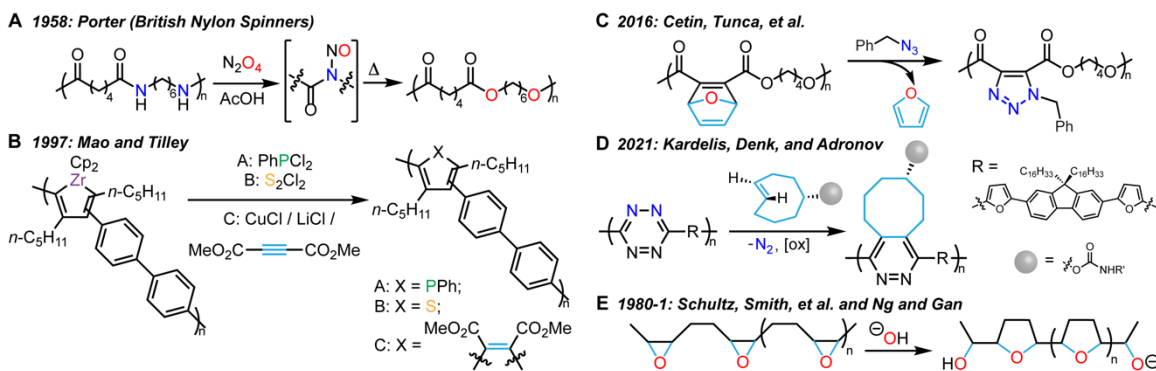


Figure 8 | Examples of combinations of elementary backbone edits (color is used to emphasize edits). A. Insertion and deletion is achieved by nitrosating nylon 6,6 yarn and then heating to produce the corresponding polyester.⁴ **B.** Zirconium is substituted for phosphorus, sulfur, and an olefin in zirconopentadiene backbone fragments treated with corresponding electrophiles.¹¹¹ **C.** Addition of benzyl azide to an oxanorbornadiene polymer fragment results in a tandem 1,3-dipolar cycloaddition and cycloelimination of furan.⁵³ Formally, these transformations result in an insertion of azide and deletion of furan. **D.** Inverse-demand cycloaddition followed by nitrogen elimination is utilized to insert substituted trans-cyclooctenes and delete N₂ from a polymer with a tetrazine fragment.⁵⁴ **E.** Cyclization and de-cyclization is achieved through a cascade ring opening of epoxides where the stereochemical outcome is determined by the stereochemistry of the starting epoxidized polymer.^{189,190}

results in deletion. Specifically, Cetin, Tunca, and coworkers demonstrated that benzyl azide undergoes a 1,3-dipolar cycloaddition with oxanorbornadienes, followed by a Diels-Alder cycloelimination of furan.⁵³ Formally, this reaction inserts azide and deletes furan from the starting polymer. The reaction proceeded with conversions of 75-99% at 20–40 °C—lower temperatures than normally required to eliminate furan from oxanorbornadienes.⁵³ Similarly, Kardelis, Denk, and Adronov utilized IDC to perform insertion of various trans-cyclooctenes with tetrazines on conjugated polymers, followed by deletion of N₂ and subsequent oxidation to furnish the final polymer structure.⁵⁴ This methodology allowed for quantitative cycloaddition of various substituted *trans*-cyclooctenes; moreover, compared to starting polymers, the modified one displayed substantial hypsochromic absorption shifts and increased emission intensities.⁵⁴

Another class of non-degenerate combinations of edits involves cyclization and de-cyclization. In one set of examples, cascade epoxide openings are used to cyclize and de-cyclize a polymer backbone and ultimately form backbone-embedded tetrahydrofuran rings (Figure 8E).^{189,190} Smith, Schultz, and coworkers demonstrated that depending on the starting stereochemistry of the epoxidized polymer, both the *threo* and *erythro* configuration of the rings are accessible (Figure 8E).¹⁸⁹ The polymers with *threo* configuration were hypothesized to adopt more helical structures, which enabled them to complex ions, in a manner reminiscent of crown ethers. On the other hand, the *erythro* configuration was unable to complex ions—a fact attributed to a more extended polymer conformation.

While reports of combinations of different elementary edits remain relatively scarce, the examples we described above give us a glimpse of the vastness of possibilities for polymer backbone transformations. Thus, the ability to compound edits opens the door to new polymeric structures that could not be prepared by direct polymerization, and properties that could advance emerging technologies. The promise of complex editing of polymer backbones motivates further development of tandem or cascade reactions that could proceed efficiently and precisely in the context of polymers.

Remaining Big Questions

By defining the field of polymer backbone editing, we hope to stimulate further development of transformations of one class of polymers into another. The examples laid out in this review describe key precedents for backbone editing and help to define trajectories for exciting future research in this field. We divide these trajectories into five main categories:

- Development of new backbone editing transformation chemistries
- Development of methods to control regio- and stereo-selectivity of backbone editing
- Elucidation of neighboring group effects in backbone editing
- Connecting backbone editing to a broader range of stimuli
- Applications of backbone editing.

Development of New Backbone Editing Transformation Chemistries

Compared to the wealth of known organic transformations, the number of examples of polymer backbone editing is miniscule. As new chemistry is developed, the editing “toolbox” will naturally expand as well. That said, for research that specifically targets polymer backbones, we find it helpful to have several simple criteria that the chemistry should fit:

- (1) An ideal backbone editing transformation produces a single product with minimal side reactions.
- (2) Substantial differences between pre- and post-editing material properties are desirable.
- (3) Chain-scission during editing should be avoided (unless degradation is the objective).

While these criteria are not absolute, they should accelerate the development of new edits and maximize their potential application, a subject we discuss below.

Development of Methods to Control Regio- and Stereo-Selectivity of Backbone Editing

Control of regio- and stereo-isomerism is crucial to tune polymer properties (e.g., the thermomechanical properties of polypropylene and electronic properties of poly(3-hexylthiophene)).^{191,192} Consequently, regio- and stereo-selectivity of editing transformations will enable control over the properties of the edited materials. As is the case in small molecule chemistry, the selectivity could emerge through catalyst or substrate control; furthermore, the mechanism of a transformation could enforce stereo-specificity in some cases (e.g., in pericyclic reactions). More particular to polymers is the consideration of neighbor effects (see discussion below), as well as the challenge inherent in modifying specific repeat units along the polymer backbone. Regardless of the source of regio- or stereo-selectivity, research in this area to enable greater precision of polymer backbone editing is essential to advance its application.

Elucidation of “Neighbor” Effects in Backbone Editing

Theoretically, an editing transformation at one repeat unit could alter the reactivity at adjacent ones, influencing both regio-/stereo-chemical outcomes as well as the kinetics of subsequent edits. Elucidating these effects would allow for a better understanding of how mechanisms differ between small molecules and polymers and potentially produce unique polymer structures. For example, a cascade reaction could produce unique block copolymers if initial reactivity could be targeted to specific sites along the backbone.

Connecting Backbone Editing to a Broader Range of Stimuli

Aside from developing new editing chemistries, connecting them to different stimuli is an important area for future research. For example, if light, heat, mechanical force, or electrical current could be channeled to induce backbone editing, the ensuing and potentially colossal

change in polymer properties would make for a powerful new mechanism to extract stimulus-response from materials. Given the broad utility of stimulus-responsive materials, we see a lot of potential for backbone editing in this context.

Applications of Backbone Editing

Editing the backbones of polymers presents new opportunities in biomedical, robotics, and space technology fields, as well as up- and re-cycling of commodity plastics and rubber materials. For some biomedical, robotics, or space applications, where direct human intervention may be challenging, materials that could undergo stimulated or programmed backbone editing (with concomitant property changes) would be quite valuable. In the realm of polymer sustainability, editing offers new ways to improve polymer properties (upcycling) or render the materials depolymerizable (chemical recycling). Unfortunately, commodity polymers, such as polyethylene, lack much of the functionality needed for current editing transformations. Furthermore, for each of these approaches, an ideal transformation would be chemo-selective and done in the polymer melt or during extrusion to allow for processing of materials that contain plasticizers and contaminants and to avoid solvent use, respectively. Thus, development of new methods of editing is crucial to advance polymer editing in upcycling/recycling applications.

Conclusion

A number of elegant and powerful examples of polymer backbone editing have been reported during the last century. A key aim of this review was to coalesce these examples into a well-defined field, with both a solid conceptual foundation and clear directions for further development. Interdisciplinary efforts—e.g., between polymer science, organic chemistry, and catalysis—will both be critical to the development of polymer backbone editing and help to build more bridges between the different disciplines involved. Thus, we hope that this review will stimulate scientific progress that will ultimately accelerate technological progress that benefits our society at large.

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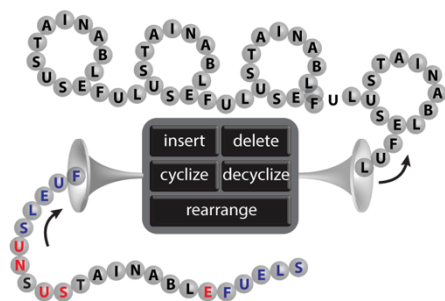
Author contributions

All authors contributed to researching data, discussion of content, writing, editing, and reviewing this manuscript.

Competing interests statement

A.V.Z. and R.A.J.D. are co-inventors on a PCT patent and provisional US patent covering research discussed in this work, filed through the University of North Carolina at Chapel Hill (PCT application no. PCT/US22/49090 and US application no. 63/278,283). A.J.K., S.E.T., and M.R. declare no competing interests.

Graphical abstract



ToC blurb

Polymer backbones and their editing are at the root of polymer function and sustainability. This Review defines the concept of polymer backbone editing, categorizes a century's-worth of research in this area, and outlines future directions for this field.