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Introduction

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Ladder polymers are double- or multiple-stranded polymers in which the adjacent monomeric units are connected by two or more bonds [1]. The repeat units of ladder polymers feature conformationally flexible or rigid, conjugated or nonconjugated rings; alternatively, the two strands in a ladder polymer could be held by noncovalent interactions, including hydrogen bonding, metal–ligand coordination, ion pairing, or van der Waals force. Ladder polymers represent a unique macromolecular architecture in that all other architectures are single stranded. While much less common than single-stranded structures, the concept of ladder polymers dates back to the early history of macromolecular science. Staudinger, recognized as “the father of macromolecular chemistry,” first proposed the possibility of forming ladder-type polymers almost a century ago [2]. He hypothesized that ladder-type poly(cyclopentadiene) could be formed via repeated cycloaddition of cyclopentadiene, although this process is thermodynamically unfavorable.

Active pursuit of ladder polymers first flourished in the 1960s, driven by the expectation of improved thermal, chemical, photochemical, and mechanical stability compared to their linear polymer analogues. Ladder polymers can be generally synthesized by direct ladder polymerization or by “zipping up” a single-stranded precursor polymer via reactive pendants or by complexation or linkage of two polymer strands (Scheme 1.1) [3–7]. Early syntheses explored both strategies, zipping up linear, conformationally flexible precursor polymers or multifunctional polycondensation to form heterocycles. But those exploratory attempts have all resulted in insoluble, intractable, and, in some cases, pyrolyzed materials, making structural analyses of these assumed ladder polymers a considerable challenge. For example, while the first synthesis of ladder polysiloxane was reported in 1960 [8], its structure was not rigorously characterized, and the chemistry was more complex than originally believed (with uncontrolled stereochemistry in siloxane formation) [9]. Decades later, only ladder-type oligosiloxanes up to five fused siloxane rings have been isolated and characterized [10, 11]. An early review from Overberger and Moore covered the early designs and synthetic endeavors toward ladder polymers, along with discussion of several limitations and challenges in the field [3].

Ladder Polymers: Synthesis, Properties, Applications, and Perspectives, First Edition.

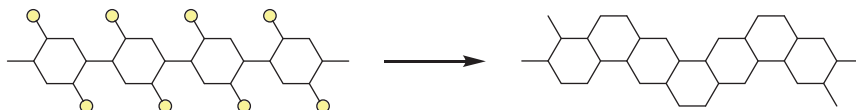
Edited by Yan Xia, Masahiko Yamaguchi, and Tien-Yau Luh.

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Ladder polymerization:



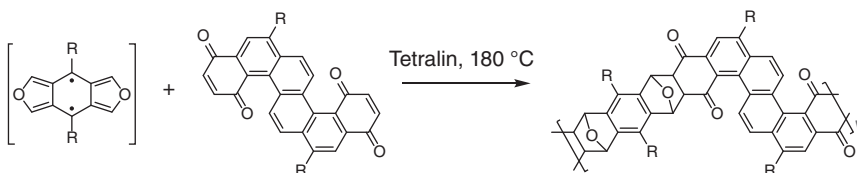
“Zipping” of a linear prepolymer:



Complexation of helical strands:



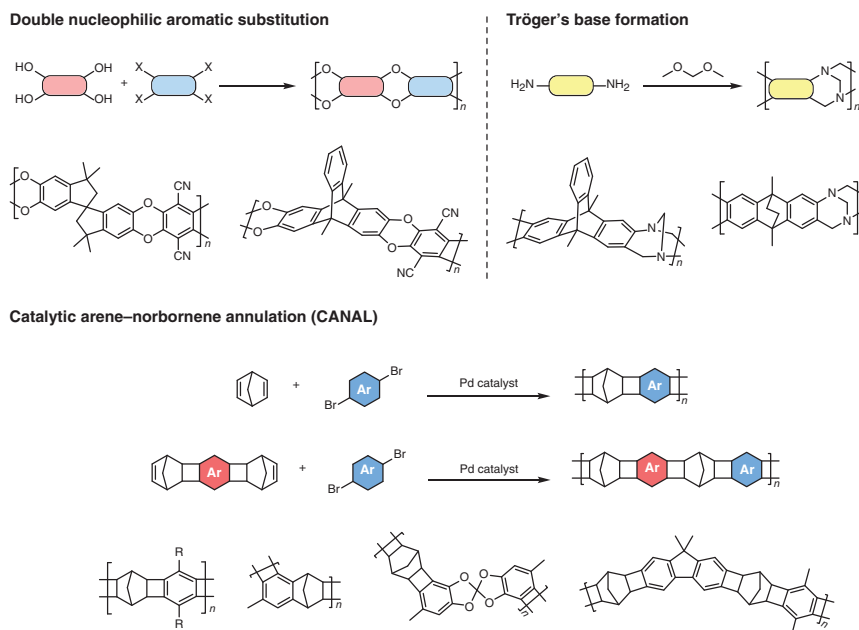
Scheme 1.1 Common strategies for ladder polymer synthesis.



Scheme 1.2 First synthesis of a soluble, unambiguously characterized ladder polymer via Diels–Alder polymerization.

The first unequivocally characterized, soluble ladder polymers were reported in 1989 by Schlüter via the Diels–Alder reaction between bisquinones and *in situ* generated bisfurans as monomers (Scheme 1.2) [12]. Diels–Alder reactions are indeed well suited for ladder polymerization due to the concerted cycloaddition to form ring structures. In the following decade, a number of creatively designed monomers were applied to Diels–Alder polymerizations [13–19]. The resulting ladder polymers exhibited rigid hydrocarbon backbones and were soluble in organic solvents when substituted with flexible alkyl groups, allowing complete spectroscopic and chromatographic analysis of the polymers. Interestingly, some of these nonconjugated ladder polymers can also be aromatized to form conjugated ladder polymers [20, 21].

In the 2000s and 2010s, McKeown and Budd achieved the polycondensation of tetrafluoro-dicyanobenzene and biscatechols via double nucleophilic aromatic substitution, as well as that of bisanilines via Tröger’s base formation, to form a new type of ladder polymer that is soluble in organic solvents without the necessity for long alkyl substituents (Scheme 1.3) [22, 23]. These polymers generate abundant microporosity in the solid state due to the frustrated packing of their rigid and contorted macromolecular chains, and are thus given the name “polymers of intrinsic microporosity (PIMs).” PIMs represent the most recent breakthrough in ladder

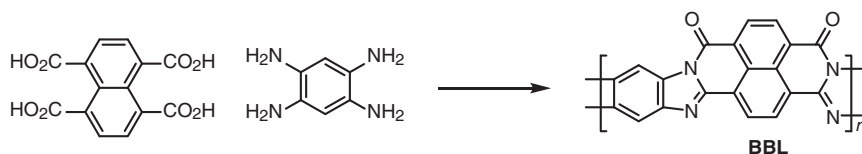


Scheme 1.3 Nonconjugated microporous ladder polymers (PIMs).

polymer development and have attracted broad attention as the next-generation membrane materials for chemical separations, particularly gas separations. Many variations on the ladder or spiro-ladder backbone structures as well as modifications of functional groups have been pursued to tune the molecular transport properties in PIM materials. In 2014, Xia and coworkers reported a catalytic ladder polymerization using norbornadiene and dibromoarenes as monomers (Scheme 1.3) [24]. This new polymerization also resulted in contorted rigid ladder polymers with abundant microporosity. The bromoarene structures and positions of bromo substituents can determine the backbone configuration, which has been found to greatly impact the separation performance of the resulting polymer membranes [25, 26].

Conjugated ladder polymers have also sparked considerable interest, owing to the expected enhanced electron delocalization in their planar π -configuration, which may lead to improved optical nonlinearity, carrier mobility, and other optoelectronic properties [4, 5, 7]. However, the ultra-strong interchain π - π interactions between two conjugated ladder polymers cause insolubility, posing significant challenges in their characterization and processing. To overcome this issue, flexible alkyl side chains are typically installed and need to be optimized to both bestow solubility and maintain favorable packing.

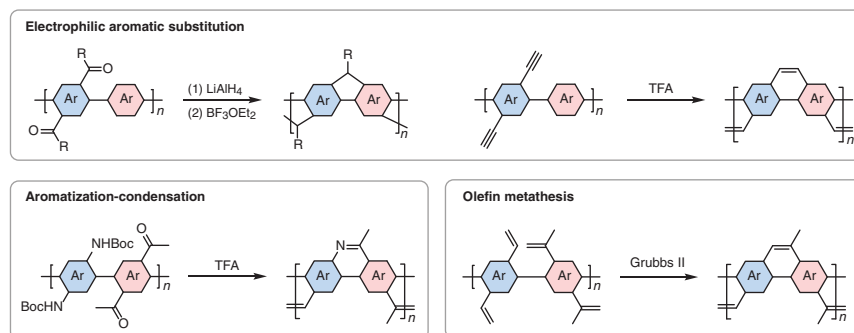
Conjugated ladder polymers can be synthesized via polycondensation or by backbone ladderization of linear conjugated polymers [7]. In 1966, Van Deusen reported the first conjugated ladder polymer, poly(benzimidazobenzophenanthroline) (BBL), via polycondensation with chemistry derived from related dye syntheses (Scheme 1.4) [27]. BBL is typically insoluble but can be dissolved in moderately



Scheme 1.4 Van Deusen's synthesis of BBL, the first reported conjugated ladder polymer.

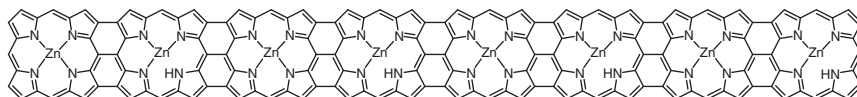
strong acids and n-doped to be conductive, leading to early organic electronic applications of conjugated ladder polymers [28, 29].

Ladder-type poly(*para*-phenylene)s have been widely explored and are synthesized by different annulation reactions of the adjacent pendant substituents of linear poly(*para*-phenylene)s to ladderize the conjugated polymer backbone (Scheme 1.5) [5, 30]. Ladder-type poly(*para*-phenylene)s exhibit strong photo- and electroluminescence, as well as high charge carrier mobilities, make them promising materials for use in light-emitting diodes and solid-state lasers [5].



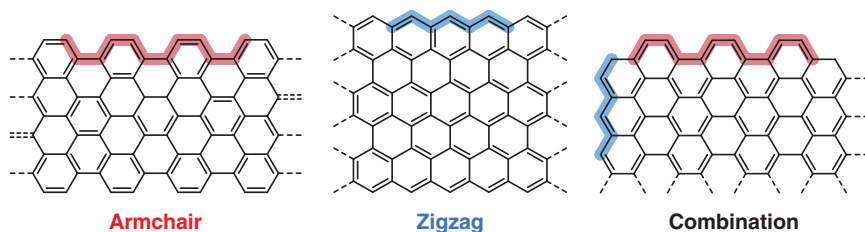
Scheme 1.5 Conjugated ladder polymers by zipping up linear conjugated precursor polymers.

Another impressive type of ladder conjugated oligomer/polymer is triply fused porphyrin ladders with up to 12 porphyrin units, which were synthesized via cyclodehydrogenation from linear porphyrin oligomers (Scheme 1.6) [31]. The porphyrin molecular ladders showed strong absorption in the IR region as a result of much more extended π -conjugation and intramolecular electronic coupling compared to the linearly linked porphyrin oligomers.



Scheme 1.6 Fused porphyrin ladder oligomer.

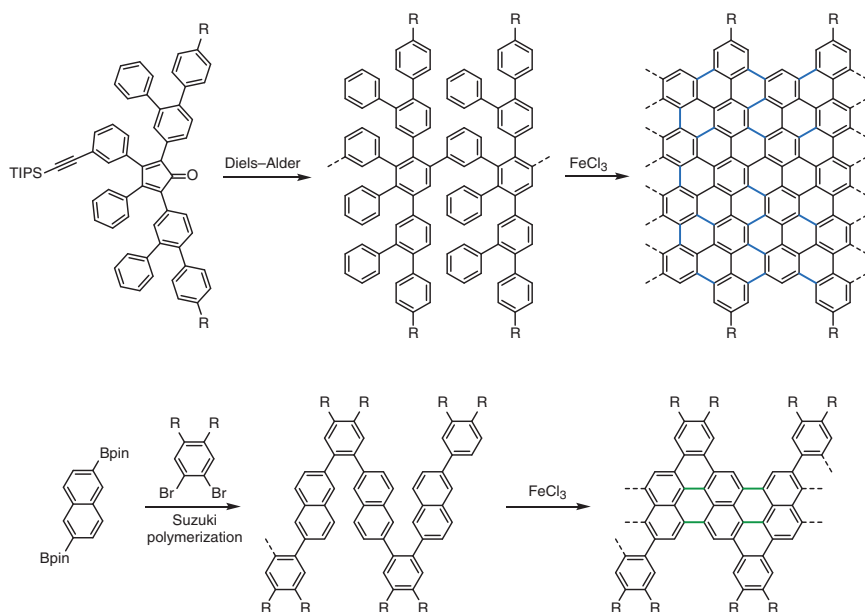
Graphene nanoribbons (GNRs) are a special class of conjugated ladder polymers that have emerged in the last two decades (Scheme 1.7). Significant advances have been made in controlling the width, topology, edge structure, and substituents of



Scheme 1.7 Graphene nanoribbons with different edge morphologies.

GNRs in order to tune their bandgap and electronic properties [32, 33]. In addition, heteroatom doping of the aromatic frameworks has emerged as another promising strategy to alter the electronic properties of GNRs [34].

The most versatile strategy for GNR solution synthesis involves designing linear polymer precursors, which are often synthesized via cross-coupling or Diels–Alder polymerizations, followed by global intrachain cyclodehydrogenation to planarize the polymers (Scheme 1.8) [33]. In addition to solution synthesis, GNRs have been synthesized on metal surfaces under ultrahigh vacuum conditions [37]. This procedure typically involves surface-assisted dehalogenative polymerization, followed by surface-assisted cyclodehydrogenation at elevated temperatures. On-surface synthesis has not only enabled new atomically precise GNR structures that are often inaccessible or uncontrolled via solution synthesis but also allowed molecular visualization of such GNRs with atomic resolution. This approach,



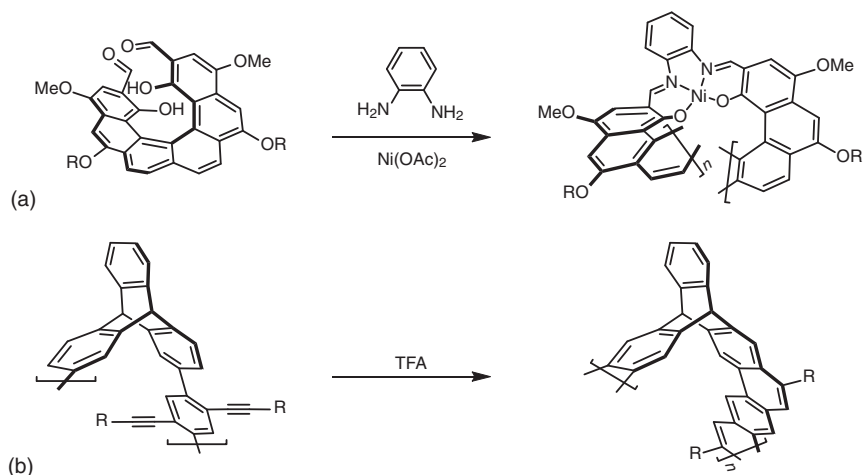
Scheme 1.8 Examples of graphene nanoribbon synthesis via Diels–Alder polymerization [35] or Suzuki polymerization [36] followed by cyclodehydrogenation.

however, requires expensive and complicated instrumentation and a high purity of monomers and is limited in scale.

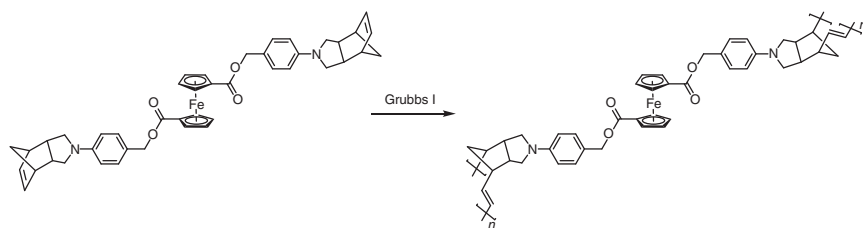
DNA can be considered a naturally existing ladder polymer, wherein the two strands are held together by hydrogen bonds between the base pairs ($A \cdots T$ and $G \cdots C$). Given the indisputable importance of DNA to all life, chemists have been fascinated by its double helical structure since its discovery. While a large variety of helical polymers have been synthesized, considerably fewer double-helical structures have been reported. Almost all the examples consist of two helical strands of oligomers, termed *helicates*, which are complexed via metal–ligand, hydrogen bonding, and salt bridge interactions [38]. The design of *helicates* leverages the geometrical coordination preference of metal ions to organic ligand strands and hydrogen bonding moieties [39]. Depending on the association strength and external conditions, *helicates* can reversibly associate and dissociate, exhibiting dynamic equilibria.

Recognition and replication of sequence information represent the most vital functions of DNA double helices, and progress has been made toward realizing such functions in synthetic systems. In 1991, Lehn and coworkers achieved the induction of one-handed helicity in double-stranded *helicates* by using optically pure ligands [40]. In 2008, Yashima and coworkers reported sequence and length-specific complementary double helix formation in short *m*-terphenyl oligomers with chiral amidine or achiral carboxyl substituents [41]. More recently, Hunter and coworkers described the replication of sequence information from a mother strand to the complementary strand in duplex formation using triazole oligomers [42].

Helicity does not only arise from single-stranded polymers, and structurally rigid ladder polymers can also adopt helical geometries. One-handed twisting conjugated ladder polymers were first synthesized by Katz in 1996 through metal–ligand coordination (Scheme 1.9a) [43, 44]. Since then, other π -conjugated helical ladder polymers



Scheme 1.9 Examples of helical (a) conjugated and (b) nonconjugated ladder polymers with one-handedness.

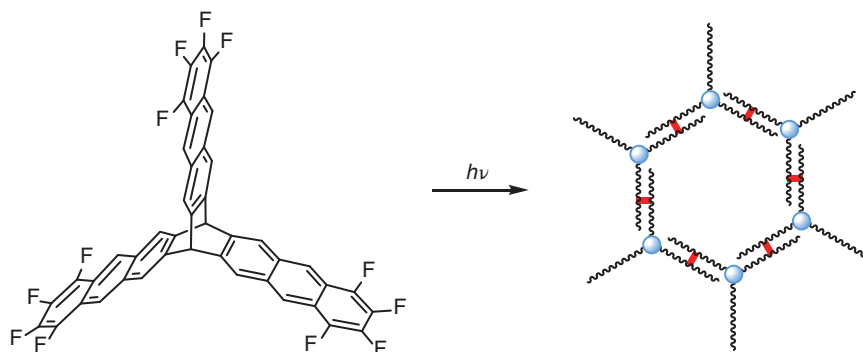


Scheme 1.10 An example of ladderphane.

comprised of fused aromatic rings (“polyhelicenes”) have been synthesized [45, 46]. Recently, helical nonconjugated ladder polymers have also been synthesized via the intramolecular cyclization of chiral triptycenes (Scheme 1.9b) [47]. Helical ladder polymers with controlled chirality may find applications in chiral separations and as circularly polarized luminescence materials.

Another type of covalent double-stranded polymer is termed ladderphane, developed by Luh [48]. The monomers for ladderphanes consist of two identical or different polymerizable groups (most often norbornene derivatives) that are linked together covalently. Ladderphanes are formed via direct simultaneous two-strand polymerization (for one example, see Scheme 1.10) or polymerization of one polymerizable group followed by a second polymerization of the other pendent polymerizable group (if the two polymerizable groups in the monomers are different).

Ladder polymers are characteristic in their backbone structures consisting of more than one strand to connect their repeat units, and further extending these polymers laterally would result in 2D architectures. Recent pioneering advances by Schlüter, King, and others have enabled the creation of such a new class of 2D polymers with topologically planar repeat units [49–53]. Structurally rigid tri-fold monomers have been elegantly designed to undergo covalent in-plane growth in layered single crystals or monolayers at an air/water interface rather than irregular 3D crosslinking (Scheme 1.11). Many potentially unusual properties and behaviors



Scheme 1.11 Example of a tri-fold monomer that forms a crystalline, 2D ladder polymer upon irradiation. Red lines indicate bonds formed via [4+4] cycloaddition between monomer units [50].

arising from this new polymer topology remain to be explored and discovered, just like the many interesting types of ladder polymer described in this book.

1.1 Perspective

A variety of fascinating ladder polymers are presented in this book, but the examples of ladder polymers are still far less than single-stranded polymers. While many more double-stranded ladder structures could be conceived, their access is ultimately limited by the available synthetic methods. Remarkably selective and high-yielding chemistry is always required for the synthetic strategies of ladder polymers, whether it is spontaneously forming two chemical bonds during a ladder polymerization or cyclizing all the repeat units with their neighboring units or complexing two strands of polymers together. For ladder polymerization, the Diels–Alder reaction has been a reliable “go-to” method thanks to its concerted mechanism, although other cycloaddition chemistries may also be suitable for this purpose, especially with the aid of efficient catalysts. Generating ladder polymers by cyclizing neighboring repeat units (the “zipping-up” strategy) or by bringing two single-stranded polymers together also sets demanding challenges on the chemistry being used. Efficient and selective “click” chemistries developed over the last two decades may prove to be useful in this context. Regardless of what type of chemistry is used, the design of monomer or polymer structures is key to electronically and spatially favoring the bond formation. We also remain rather limited in our ability to control the molecular parameters of ladder polymers. Controlled/living polymerization has led to tremendous progress over the last several decades in the synthesis of single-stranded polymers with various architectures and with controlled molecular weight, end groups, tacticity, and certain monomer sequences. These molecular parameters have been used to tune the properties of single-stranded polymers. However, such a high level of control has not yet been achieved for ladder polymer synthesis. One challenge in realizing this goal is to conduct ladder polymerizations through a chain-growth rather than a step-growth mechanism, which would require the growing ladder chain end to be more reactive than an initiating monomer. Catalyst transfer polycondensation [54], which has been successfully applied to the controlled synthesis of conjugated polymers, and other chain-growth polycondensation strategies [55], may be applied to future ladder polymerizations. Being able to control the functional end groups and molecular weights of ladder polymers could facilitate their integration with other materials or surfaces and enable the synthesis of entirely new ladder architectures, which may lead to more complex assembly structures, materials with multidimensional charge transport properties, or macromolecular filters with well-defined pores.

Because no chemistry is perfect, all ladder polymers almost certainly contain non-ladder structural defects. Under what circumstances, and to what extent, do these defects matter? For example, they may have a substantial effect on the optoelectronic properties of conjugated ladder polymers or the ability of double-stranded polymers to store and transcribe information. In other cases, a small fraction of

linear defects may not affect the surface areas or thermomechanical properties of ladder polymers. Rigorously studying the effects of these defects would offer valuable insight into the unique properties of ladder-like architectures. What types of defects are the most detrimental? What is the minimum required ladder length to exhibit the characteristic properties of ladder structures? Although the quantitative analysis of a small fraction of defects in polymers can be challenging, investigating model reactions on small molecules and oligomers may provide useful information.

The development of ladder polymers can also be hampered by their challenging processing, characterization, and analysis. The glassy nature and often low solubility of ladder polymers lead to difficulties in common melt and solution processing techniques, which will require creative engineering designs to overcome. In regard to characterization, the limited bond flexibility (in some cases, extreme rigidity) of these polymers leads to large persistence lengths and likely also results in anisotropic chain conformations. While light, X-ray, or neutron scattering can provide some information about the dimensions of single ladder polymer chains and their packing, appropriate models are yet to be developed for the analysis of scattering data of ladder polymers. In addition, the classical concept of chain entanglement in polymer science likely does not apply to ladder polymers, as we typically cannot access their molten state and the total lengths of many reported ladder polymers can be below their entanglement molecular weights. The highly glassy nature of these polymers under most analysis/application conditions can lead to many potential trapped kinetic states and local dynamics, which can also complicate analysis.

The ongoing discovery of new applications for ladder polymers requires us to study and harness their unique chemical properties broadly. For example, their restricted conformations should translate to high mechanical strength and a reduction in the entropic cost of forming hierarchical assembled structures, potentially leading to their use as building blocks for molecular machines and macroscopic materials. Similarly, the structural rigidity of ladder polymers should promote thermal conductivity due to reduced phonon scattering. To translate molecular properties into desirable macroscopic properties, however, we must control the chain alignment and connectivity at the mesoscale, which would be facilitated by chemistry that can precisely control the molecular parameters. In fact, the intrinsic mechanical and thermal properties of individual ladder chains at the single-molecule level still remain to be explored.

Another potential application of ladder polymers is in self-healing materials, a research area that has grown considerably in recent years. But the concept of facilitated bond “healing” in ladder polymers was first proposed decades ago. It is believed that once a chemical bond is ruptured, bond reformation can occur more readily if the two segments are held near each other (as is possible in a ladder structure) rather than diffusing apart. However, such facilitated “healing” in a ladder polymer has not yet been demonstrated.

As we continue to devise novel ladder structures, we can turn to nature for inspiration. Although there are no known examples of naturally occurring covalent ladder polymers, there are astonishing ladder structures in natural products. Anaerobic ammonium oxidizing (“anammox”) bacteria produce a variety of ladderanes

as a significant fraction of their membrane lipids [56]. These ladderane lipids contain ladder-type motifs comprised of fused cyclobutanes and other rings in their hydrophobic tails. While the biological origin and function of these molecular ladders remain a mystery, some evidence suggests that they form densely packed membranes that limit transmembrane diffusion of toxic or valuable byproducts of anammox catabolism [57, 58]. The highly strained structures of cyclobutane ladders have inspired chemists to explore their non-natural reactivity and generate unprecedented polymers with ladder side chains that transform into conjugated polymers in response to mechanical force [59]. The response of ladder structures to other stimuli or environmental conditions (including heat, irradiation, electric fields, reactive chemicals, or biologically relevant molecules) may be investigated in time as well.

The field of ladder polymers has gradually advanced since the early attempts at their synthesis in the 1960s. Over time, we have witnessed a plethora of applications of these polymers in opto-electronics, chemical separations, and other energy technologies. Perhaps even more significantly, ladder polymers have provided us with inspiration to further advance our ability to understand, assemble, and manipulate molecules. To the extent that the complexity of ladder polymers complicates their synthesis and characterization, it likewise motivates us to continue pursuing these intriguing molecules. We envision countless more developments and unexpected discoveries of ladder polymers as collaborations between chemists, physicists, and engineers continue to emerge in the coming decades.

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