

**Photoredox Diels–Alder Ladder Polymerization**

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Ladder polymers are synthetically challenging targets that comprise a sequences of rings in which each repeat unit shares at least two atoms with the adjacent one. Ladder polymers with sp^3 -hybridized backbones feature kinked structures with restricted bond rotation. Such ladder polymers are typically synthesized through a mechanism that allows simultaneous formation of both bonds during polymerization, such as the Diels–Alder cycloaddition. Prior Diels–Alder polymerizations yielding ladder polymers required elevated temperature and/or pressure to achieve the desired reactivity, and the resulting products include aromatic linkages within the backbone. Here, we show that photoredox catalysis provides access to unique ladder polymers with sp^3 backbones under mild reaction conditions. We design 2-arylbutadiene monomers that enable propagation of the cyclohexene formed by each successive cycloaddition by stabilizing the required radical cation. The polymerization achieves molecular weights up to 4,400 g/mol with various electron-rich 2-aryl butadiene monomers. The resulting products may also be treated as macromonomers to form ladder bottlebrush polymers through a cationic polymerization. This report represents the first example of applying photoredox catalysis to the synthesis of ladder polymers and yields a novel sp^3 -rich ladder polymer structure.

Introduction

Ladder polymers, which have two continuous junctions along the polymer backbone, have long enticed and puzzled chemists with their distinctive structures and challenging synthesis.¹ Because each repeat unit shares two atoms with the adjacent one, forming an uninterrupted sequence of rings,² ladder polymers have significantly limited degrees of rotation. These restricted conformations prevent efficient chain packing and can lead to materials that are intrinsically microporous, with applications in gas-phase separation, water purification, and chemical warfare agent detoxification.³ The Diels–Alder cycloaddition presents an attractive synthetic route to ladder polymers because of the concerted nature of the ring-forming reaction. In 1926, Staudinger posited the first synthesis of a ladder polymer through the repeated cycloaddition of cyclopentadiene, and found that heating dicyclopentadiene at 200 °C for 90 h yielded an insoluble white powder that depolymerized to cyclopentadiene at 500 °C (**Figure 1a**).⁴ While Staudinger's proposed polymerization involves a thermodynamically disfavored [2+2] cycloaddition, a [4+2] cycloaddition, which had not yet been reported by Diels and Alder,⁵ is more likely. Schlüter used the Diels–Alder cycloaddition to prepare the first soluble, fully characterized ladder polymer using a highly reactive diene that was generated in situ.^{6,7} Despite the popularity of the Diels–Alder reaction for

the synthesis of ladder polymers, efficient polymerization often requires high-temperature or hyperbaric⁸ reaction conditions. Since then, other reactions commonly used to form both bonds along the polymer backbone include Pd-catalyzed annulation,⁹ S_NAr polycondensation,¹⁰ and Tröger's base formation.¹¹ Notably, all previous reports involve aromatic monomers, so the resulting ladder polymers include some sp^2 atoms along the backbone even though they are not fully conjugated.

We envisioned that photoredox catalysis could be used to access ladder polymers with saturated backbones without elevated temperature or pressure. The advent of photoredox catalysis in polymer chemistry has enabled spatiotemporal control and mild reaction conditions.¹² Photoredox catalysis has been applied to many classes of polymerization,¹² including RAFT,^{13–15} ATRP,^{16,17} ROMP,^{18,19} ROP,²⁰ and cationic polymerization of vinyl ethers.^{21,22} Surprisingly, photoredox catalysis has not yet been applied to the synthesis of ladder polymers. We were inspired by the photoredox Diels–Alder cycloaddition reported by Yoon and coworkers, in which an electronically mismatched diene and dienophile react through a radical cationic pathway (**Figure 1b**).²³ In this small-molecule example, the dienophile must contain an electron-rich aryl group to allow oxidation by the photoredox catalyst.²⁴ However, the unactivated alkene in the product derived from isoprene cannot be oxidized, preventing further cycloadditions. We hypothesized that the diene could be modified to support subsequent oxidation of the cycloadduct, thus enabling multiple sequential Diels–Alder reactions to ultimately form a ladder structure (**Figure 1c**). We envisioned that a readily oxidized 1-arylcyclohexene could serve as the initiator, while 2-arylbutadiene monomers would produce cycloadducts with activated alkenes capable of propagation by the radical cation

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† Footnotes relating to the title and/or authors should appear here.

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Diels–Alder mechanism. Unlike the ladder polymers accessed by prior approaches, including Diels–Alder polymerizations, the

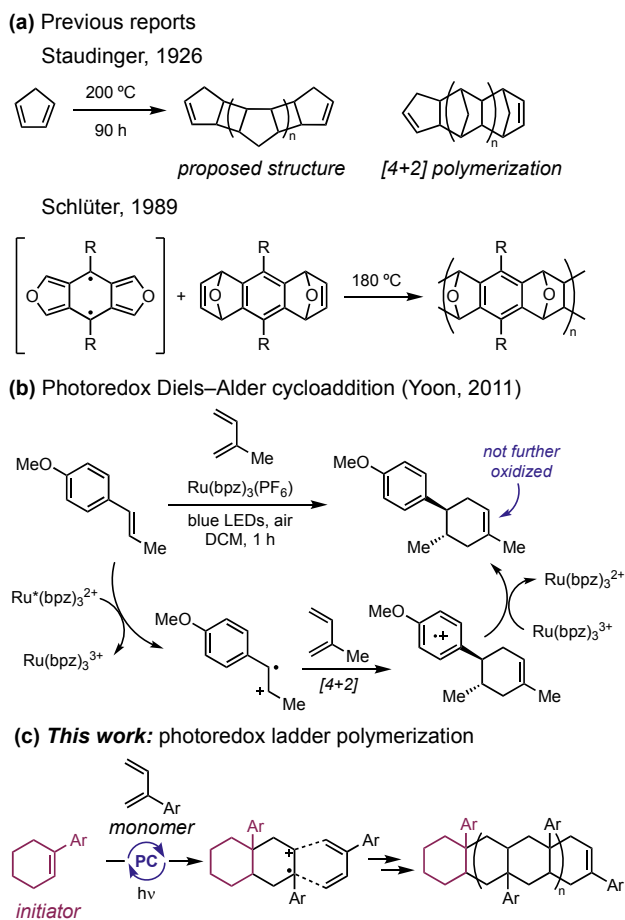


Figure 1. (a) Previous attempts and successful reports of ladder polymerization based on cycloaddition reactions. (b) Radical cation Diels–Alder of *trans*-anethole and isoprene using photoredox catalysis. (c) Our proposed ladder polymerization via photoredox catalysis.

resulting polymer would possess a fully sp^3 -hybridized backbone with the exception of the propagating terminus. The properties of such saturated ladder polymers are entirely unknown. Such a polymerization could also follow a chain-growth mechanism, distinct from other Diels–Alder polymerization, which are step-growth in nature. Herein, we report the first photoredox ladder polymerization, explore the scope of this reaction, and demonstrate the ability to further polymerize the resulting products to increase their molecular weights.

Results and Discussion

We first sought to confirm that the expected product of the proposed Diels–Alder cycloaddition, a 1-arylcylohexene, can serve as a dienophile for subsequent propagation. Using cyclic voltammetry, we studied the oxidation of *p*-methoxyphenyl cyclohexene **1** (Figure 2a). Cyclohexene **1** underwent an irreversible oxidation event at +0.85 V vs. ferrocene/ferrocenium, suggesting that it has an even lower

oxidation potential than *trans*-anethole, Yoon's model substrate (+0.9 V).²³ These comparable oxidation potentials suggest that the electronics of **1** would support a radical cation cycloaddition. However, **1** is also a trisubstituted alkene, making it more sterically hindered than *trans*-anethole. To confirm that the radical cation derived from **1** can undergo cycloaddition, we subjected **1** and excess isoprene to various photocatalysts and oxidants (Figure 2b). Gratifyingly, **1** underwent successful cycloaddition with several oxidizing photocatalysts (see Electronic Supplementary Information (ESI), Table S1). The structure of adduct **2** was confirmed by both mass spectrometry (MS) and ¹H nuclear magnetic resonance spectroscopy (NMR). As expected, the unactivated alkene in **2** did not undergo further propagation, but we anticipated that these photoredox conditions could be extended to the proposed ladder polymerization with appropriate monomers. These results demonstrate that a 1-arylcylohexene can serve as a dienophile in the radical cation Diels–Alder cycloaddition promoted by photoredox catalysis, supporting the propagation step of the proposed ladder polymerization.

Emboldened by these small-molecule results, we sought to apply these conditions to polymerization using 2-aryl-1,3-diene monomers in place of isoprene. We hypothesized that the electronics of the aryl group would influence its ability to support subsequent oxidation of the terminal cyclohexene and

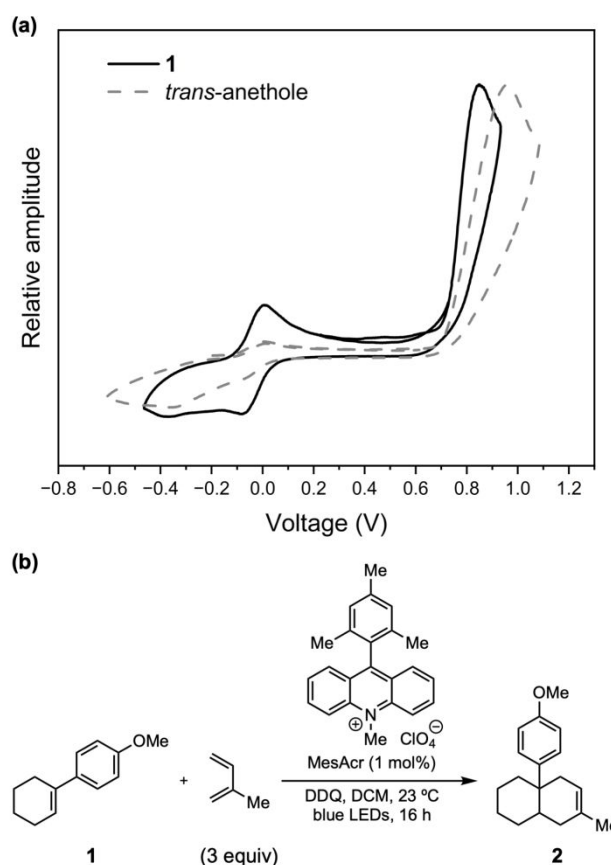


Figure 2. (a) Cyclic voltammetry comparing **1** and *trans*-anethole. Conditions: 0.1 M TBAPF₆ in acetonitrile, Pt working electrode, Pt auxiliary electrode, AgCl reference electrode, and ferrocene as a reference. (b) Small-molecule test reaction with isoprene.

thus undergo propagation. Initially, we performed polymerization experiments with cyclohexene **1** as the initiator and 5 equivalents of *p*-methoxyphenyl diene **3a** (Figure 3a). These conditions resulted in low-molecular-weight oligomers with M_n 490 g/mol (\bar{D} 1.4) (expected 988 g/mol) as indicated by gel permeation chromatography (GPC). Additionally, during vacuum distillation of **3a** at elevated temperatures, we observed side products arising from a single Diels–Alder cycloaddition, suggesting reactivity outside of the radical cation manifold. Fortunately, replacing the methoxy group with a silyl ether suppressed the thermal reactivity and improved the solubility of the products; furthermore, the silyl ether could be

deprotected for post-polymerization modifications. With 5 equivalents of TBS-protected diene **3b** relative to **1**, we obtained oligomer with M_n 780 g/mol (expected 1,488 g/mol). Further increasing the amount of monomer relative to initiator to 15:1 increased the molecular weight to 1,300 g/mol (\bar{D} 1.5, expected 4,088 g/mol) with a yield of 71% at nearly complete conversion of **3b**. The disparity between the theoretical and experimental molecular weights suggests that the polymerization is not well controlled (*vide infra*). The polymerization of diene **3b** proceeded with a variety of photocatalysts, solvents, oxidants, and at a variety of

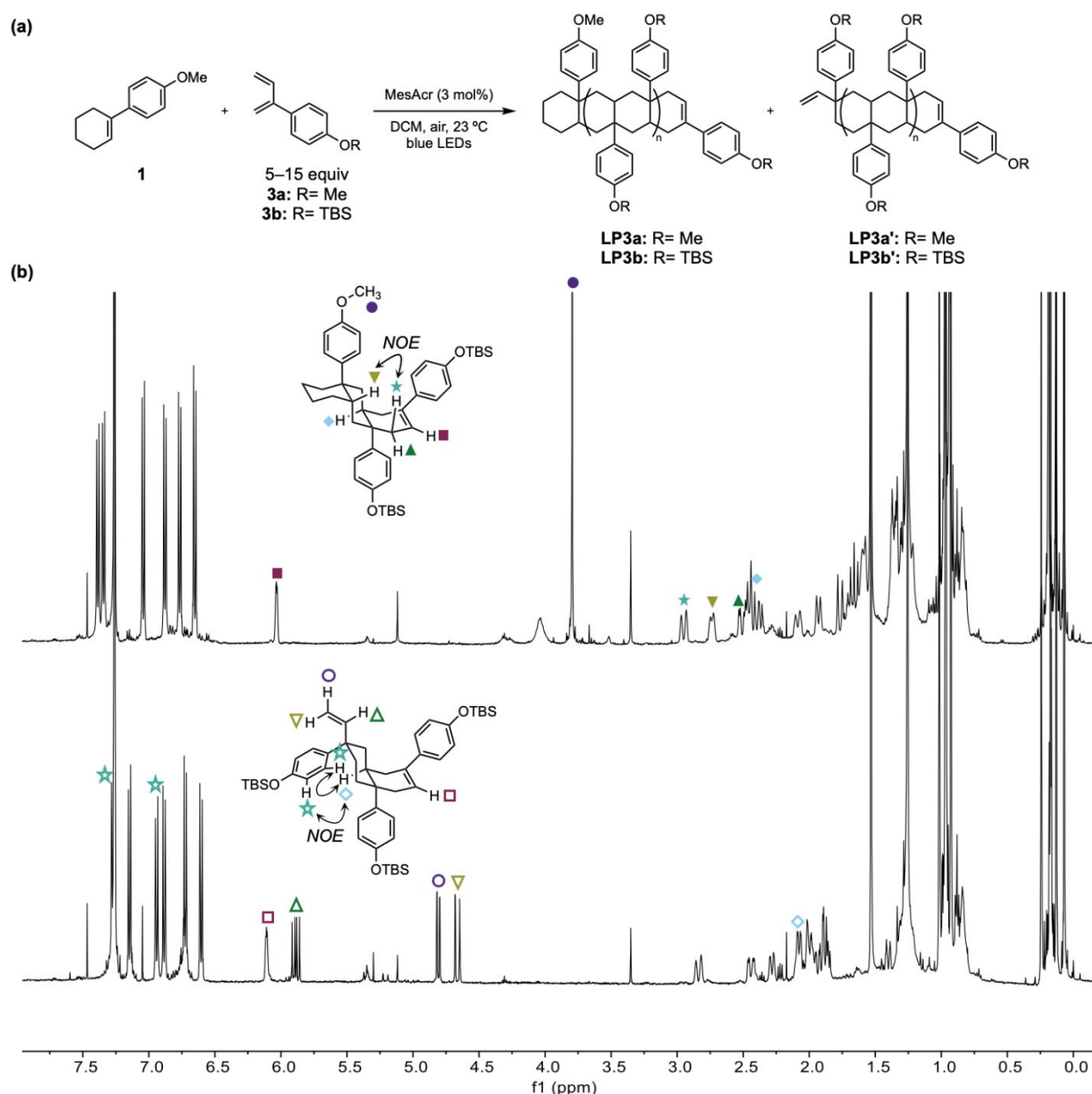


Figure 3. (a) Initiation pathways for the photoredox Diels–Alder polymerization assigned based on MALDI-TOF and NMR analysis (see ESI for details). (b) ¹H NMR spectra of the bis-addition product for both initiation pathways; see ESI for isolation procedure and additional spectroscopic data. Key NOE interactions are indicated.

concentrations, but with minimal effect on the molecular weight containing **1**, we also observe Diels–Alder adducts lacking **1** and

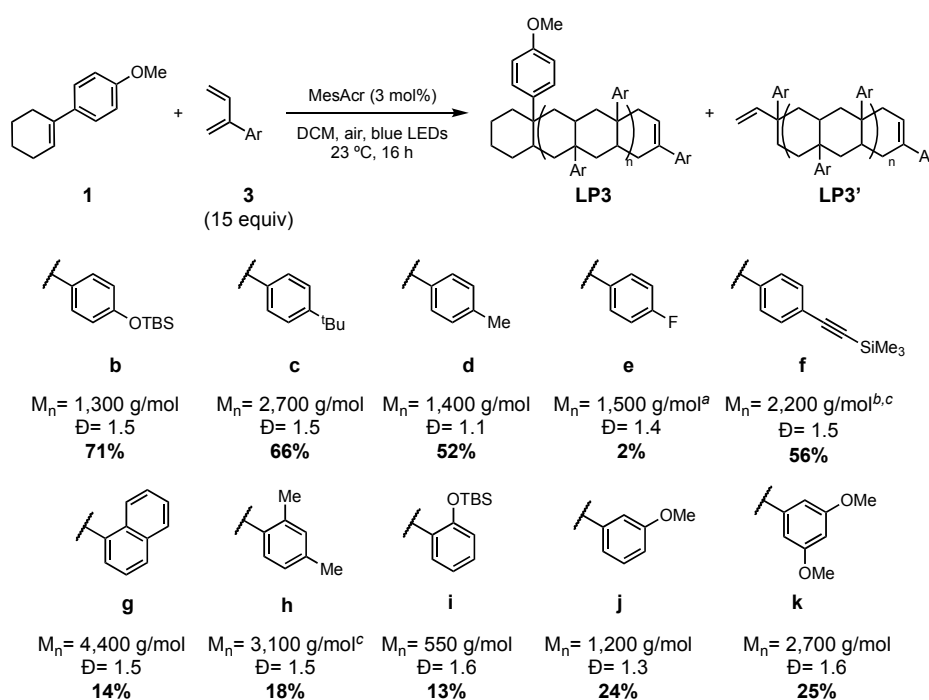


Figure 4. Scope of the Diels–Alder polymerization. Polymerizations were conducted with a 1:15 initiator/monomer ratio and precipitated into 7:1 methanol–water. The resulting polymer was analysed using GPC–MALS. ^aPolymer did not precipitate into methanol; in these cases yield and molecular weight are based on the supernatant. ^bNo initiator was used for this polymerization. ^cMolecular weight was determined using GPC–RI detection relative to polystyrene standards.

weight of the product (see ESI for additional conditions).

Using monomer **3b** and initiator **1**, we performed several control experiments to confirm the role of light in the reaction. We do not obtain polymer in the absence of light, photocatalyst, or diene (ESI, **Table S4**). We questioned whether the modest molecular weights arise from a competing retro-Diels–Alder process. However, when we subjected the isolated polymer to the standard reaction conditions (photocatalyst, light, no monomer), we did not observe a decrease in M_n . Under the standard photoredox conditions in the absence of **3b**, **1** undergoes [2+2] dimerization;²⁵ this side reaction is not observed when the diene is present. Interestingly, we still observed polymer formation with M_n 1,200 g/mol when **1** was not added to the reaction mixture, suggesting that the initiator is not necessary.

These observations prompted us to investigate the products of the reaction in more detail. Since ¹H NMR spectra of the polymeric products were complex, preventing detailed structural elucidation, we isolated and characterized oligomeric products formed from **1** and **3b** under the photoredox conditions. After precipitation into methanol, we separated the oligomeric products in the supernatant via preparative thin-layer chromatography and analysed their structures using 1D and 2D NMR. The products we isolated correspond to well-defined Diels–Alder cycloadducts derived from **1** and **3b** in various ratios up to DP 4. The double addition of **3b** to **1** was fully characterized and assignments for key protons in the ¹H NMR spectrum are shown in **Figure 3b**. In addition to oligomers

containing an additional monosubstituted olefin, which we assign to [4+2] cycloaddition between two dienes. Based on this assignment, we propose that the polymerization may either be initiated by **1** (forming **LP3b**) or by the diene itself (forming **LP3b'**). While **LP3b'** contains two alkenes, the monosubstituted alkene would not be oxidized by the photocatalyst, thus propagation should still occur unidirectionally. These assignments are consistent with MALDI–TOF analysis of the reaction products (ESI, **Figures S33–S35**). In the absence of **1**, masses corresponding to multiples of **3b** are observed, while polymerization in the presence of **1** yields the same set of peaks in addition to a set indicating incorporation of initiator. Initiation by the diene partly accounts for the discrepancy between theoretical and experimental molecular weights.

2D NMR was used to determine the alternating regiochemistry of addition, consistent with the literature,²³ while the nuclear Overhauser effect (NOE) was used to assign the stereochemistry of the oligomers (**Figure S71** and **S83**). Relevant NOE interactions are shown in **Figure 3b**. ¹H NMR analysis of the polymers reveals the same characteristic signals observed in the oligomers, including the cyclohexene vinyl proton at 6.1 ppm and the OMe proton of **1** at 3.8 ppm, but the presence of several peaks in each region suggests that these protons exist in a variety of environments. For example, an incoming diene can react with either the top or bottom face of the cyclohexene terminus, resulting in different diastereomers of the product. While the oligomers we isolated were predominantly single diastereomers, we cannot confirm

diastereoselectivity for the polymerization. The ^1H NMR spectra of these ladder polymers are notably distinct from those of the linear polymers synthesized from 2-aryl diene monomers using a Mg-initiated polymerization reported by Fiorito et al.²⁶

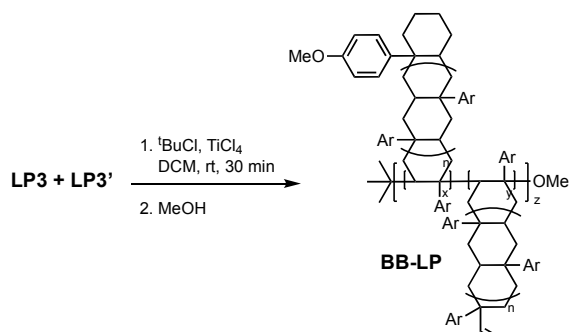
We next synthesized a library of 2-aryl diene monomers and subjected them to our optimized conditions. Polymerizations were evaluated based on the yield after precipitation into methanol and molecular weight by gel permeation chromatography (GPC). Because of the rigid structure of ladder polymers, GPC evaluation of molecular weights using polystyrene standards on GPC are generally accepted as less accurate.^{1,27} Therefore, we used GPC coupled with multiangle light scattering (MALS) to determine the absolute molecular weights of the polymers. For most dienes evaluated, GPC indicated formation of oligomeric (~1500 g/mol) species in low to moderate yields (Figure 4). **3c**, bearing a *para*-tertbutylphenyl group, provided one of the highest yields and molecular weights, most likely due to the electron-donating and solubilizing nature of this substituent. A *para*-methyl group (**3d**) also provided modest yield of an oligomer. As expected based on the radical cation mechanism, electron-poor aryl dienes such as **3e** had deleterious effects on the molecular weight, conversion, and yield. TMS-alkyne **3f** provides a handle for post-polymerization modification. Beyond substitution at the *para* position, *ortho* substituents decreased the yield of oligomer/polymer with variable effects on molecular weight. Compared to *para*-substituted arenes, 2-naphthyl (**3g**) and 2,4-dimethylphenyl (**3h**) dienes provided improved molecular weight, while sterically hindered **3i** prevented efficient polymerization. While *para*-methoxy-substituted **3a** was too reactive, undergoing background thermal reactions, meta-substituted **3j** and **3k** provided modest yields and molecular weights. Molecular weights were not significantly influenced by photocatalyst, solvent, and reaction concentration, suggesting the versatility of the polymerization (see ESI for additional conditions). Unfortunately, we were unable to find polymerization conditions that significantly increased the molecular weight of the polymers. Synthesizing ladder polymers of high molecular weights has historically been a challenge due to the limited degrees of rotation of the polymers, which leads to lower solubility.¹ Unknown termination mechanisms may account for the limited molecular weights and lower yields observed for some of the reactions. Moreover, the uncontrolled nature of initiation, wherein both **1** and **3** act as initiators, may also limit molecular weight. We do not believe solubility limits molecular weight for this class of polymers since polymerizations at 2 and 4 M resulted in similar M_n (Table S2). When we attempted to increase the molecular weight of **LP3b** by subjecting the isolated polymer to additional **3b** and photocatalyst, only a modest increase was observed (Table S5). We also speculate that the rigid, kinked conformation of these materials may render the propagating alkene sterically inaccessible after multiple cycloadditions, limiting the molecular weight of the polymers.

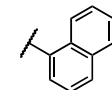
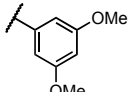
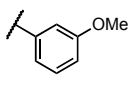
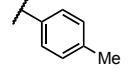
The surface areas of the ladder polymers obtained through the photoredox polymerization are modest (ESI, Figures S3-4). The microporosity of ladder polymers often increases with their

molecular weight.²⁸ Therefore, we sought to increase the molecular weight of these oligomers by using them as macroinitiators for a different polymerization mechanism. Inspired by recent reports by Swager and coworkers,^{29,30} we hoped to convert the oligomeric products of the photoredox pathway to bottlebrush ladder polymers. Unlike the ladder polymers synthesized by Swager and coworkers, the cyclic alkene of the Diels–Alder adduct is not amenable to ring-opening metathesis polymerization. Instead, we hypothesized that the cyclohexene at the propagating end of both **LP3** and **LP3'** would be sufficiently electron-rich to engage in Lewis acid-initiated cationic polymerization. A subset of polymers from Figure 4 was subjected to previously reported cationic polymerization conditions and the polymers were evaluated by GPC-MALS (Table 1). Indeed, we observed increases in molecular weight for each polymer sample. For **LP3g** and **LP3k**, we observed significant increases in molecular weight, while polymers with less electron-rich arene end groups led to more marginal increases. This reactivity provides additional support for the presence of the cyclohexene end group. Future experiments include evaluating the gas-sorption characteristics of these bottlebrush polymers and comparing them to their precursors.

Conclusions

Table 1. Cationic polymerization to synthesize bottlebrush ladder polymers.^a



Ar	LP3/3' M_n (g/mol)	BB-LP M_n (g/mol) ^b
	4,400	23,000
	2,700	16,000
	1,200	7,200
	1,400	2,300

^aPolymers were precipitated into 7:1 methanol–water. ^bMolecular weights determined by GPC-MALS.

In conclusion, we have developed mild conditions for synthesizing highly saturated ladder polymers through a photoredox Diels–Alder cycloaddition. The polymerization proceeds with a variety of photocatalysts, solvents, and electron-rich aryl diene monomers. Evidence for the cycloadduct structure of the products is obtained from NMR analysis of isolated oligomers. Although a cyclohexene initiator is incorporated into the polymers, we also found evidence for initiation by the monomer itself. Furthermore, we can exploit the resulting alkene end groups to synthesize higher-molecular-weight bottlebrush polymers through a cationic mechanism. While the polymerization is not well controlled, it likely proceeds through a chain-growth mechanism initiated or mediated by light.³¹ Future experiments include characterizing the microporosity of these polymers, comparing their microporosity to linear analogues, and investigating the polymerization kinetics.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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