

Metal-Free Preparation of Linear and Cross-Linked Polydicyclopentadiene

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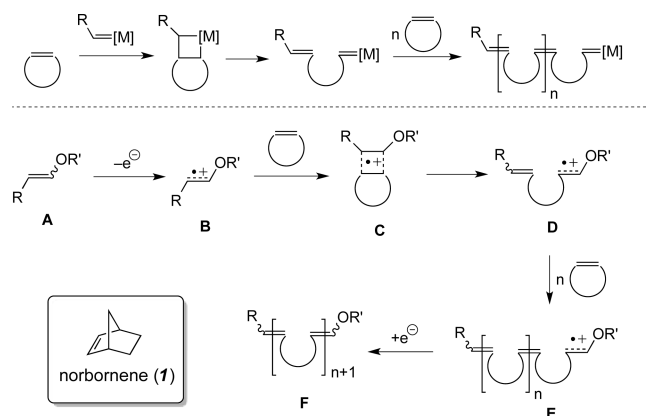
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S Supporting Information

ABSTRACT: Metal-free ring-opening metathesis polymerization (ROMP) utilizes organic photoredox mediators as alternatives to traditional metal-based ROMP initiators to allow the preparation of polymers without residual metal contamination. Herein we report studies exploring the use of *endo*-dicyclopentadiene (DCPD), a common ROMP monomer, to form linear polyDCPD and copolymers with norbornene. Subsequent cross-linking of the linear polyDCPD using thiol–ene chemistry allows for a completely metal-free preparation of cross-linked polyDCPD. Furthermore, the examination of a number of structurally related monomers offers insights into mechanistic details of this polymerization and demonstrates new monomers that can be utilized for metal-free ROMP.

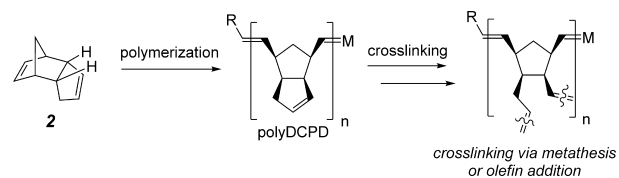
Ring-opening metathesis polymerization (ROMP) is a popular method for the preparation of a variety of functional polymers.¹ The versatility of this method has resulted in applications in diverse areas such as commodity-scale performance plastics and novel biocompatible systems for drug delivery.² Traditional ROMP initiators consist of Ru-, W-, or Mo-alkylidene complexes, along with a number of ill-defined species containing various mixtures of metal salts. Notably, each of these initiators is envisioned to proceed through the same general mechanism involving a metallacyclobutane intermediate (Scheme 1, top).

Scheme 1. (Top) Mechanism of Traditional ROMP Using Metal Initiators, and (Bottom) Proposed Mechanism of Photoredox-Mediated Metal-Free ROMP



The importance of metal-based ROMP and other related olefin metathesis processes cannot be overstated; however, in a practical sense, the presence of residual metal species in final products can limit applications or necessitate elaborate purification procedures.³ Recently, our laboratory reported the development of a metal-free method for achieving ROMP based on the single-electron oxidation of enol ether initiators using photochemically activated pyrylium salts as oxidants.⁴ We believe this polymerization occurs through a mechanism that is inherently distinct from the traditional ROMP mechanism, due in part to the absence of any organometallic species (Scheme 1, bottom). Additionally, the dynamic redox nature of the terminal enol ether results in a polymerization that can be “turned on” through the application of visible light and subsequently paused and restarted by controlling exposure to this stimulus.⁴

Scheme 2. Polymerization and Cross-Linking of DCPD



Our initial report focused on the polymerization of norbornene (1); however, our interest in preparing polymers with more complex functionality led us to examine dicyclopentadiene (DCPD, 2, Scheme 2), which in its commercially available form exists almost exclusively as the *endo* isomer. Although catalyst systems that enable the preparation of linear polyDCPD (Scheme 2) are known,⁵ many procedures produce insoluble, cross-linked polymer networks resulting from either olefin metathesis⁶ or olefin addition^{5a,b} reactions of the cyclopentene moiety. Cross-linked polyDCPD has many applications, for example, as vehicle body panels in materials that require high corrosion resistance. However, the nature of the cross-linking process results in the metal catalysts used for polymerization remaining trapped inside the final polymer, which can be problematic for certain applications. Following our initial report, we questioned whether our metal-free ROMP conditions might allow for the preparation of cross-linked polyDCPD. Such a method could

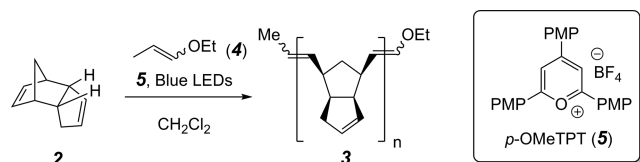
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enable access to new materials via unique cross-linking reactions and networks devoid of metal contamination.

Using our previously reported conditions for metal-free ROMP,⁴ we found that monomer **2** could be polymerized using enol ether initiator **4** and photoredox mediator **5** upon exposure to blue light (Scheme 3).⁷ Under these conditions,

Scheme 3. Preparation of Linear PolyDCPD Using Metal-Free ROMP



conversion of **2** was found to be 15%, and the polymer that was formed was of low molecular weight ($M_n = 3.8$ kDa; $\mathcal{D} = 1.1$). In comparison, the use of norbornene (**1**) as monomer often leads to >80% conversion.⁴ Notably, the polyDCPD (**3**) remained soluble in common organic solvents (e.g., THF, CH_2Cl_2 , and toluene) and showed no signs of cross-linking by ^1H NMR or GPC analysis.⁸ Control experiments further confirmed the lack of reactivity of cyclopentene under these conditions (see Supporting Information).

Attempts to optimize this polymerization to achieve higher conversion are outlined in Table 1. Independently varying the initial monomer concentration (entries 1–3) or pyrylium (**5**) loading (entry 4) resulted in no significant changes in conversion. Carrying out the polymerization at 4 °C (entry 5) gave a slight improvement in conversion, as did decreasing the initial ratio of monomer to initiator (entry 6). In all cases, the M_n values of the final polymer remained low (typically <6 kDa in each case).⁹ Notably, ^1H NMR analysis of the enol ether end group showed the presence of multiple enol ether species (see Supporting Information), which could arise from undesired side reactions that limit monomer conversion. We believed that exploring the reasons behind this poor performance would lead to the identification of additional monomers that perform well and help expand the scope of the metal-free ROMP protocol.

Table 1. Attempted Optimization of *endo*-DCPD Polymerization

entry	2:4:5 ^a	[2] ₀ (M) ^b	temp (°C)	conversion (%) ^c
1	101:1:0.07	1.26	23	13
2	102:1:0.07	1.75	23	15
3	100:1:0.07	2.80	23	13
4	102:1:0.25	1.75	23	15
5	100:1:0.07	1.75	4	19
6	51:1:0.07	1.76	23	20

^aInitial molar ratio of **2**, **4**, and **5**. ^bInitial concentration of **2** in CH_2Cl_2 . ^cConversion determined by comparison of monomer and polymer peaks by ^1H NMR spectroscopy.

Initially, we investigated whether the presence of monomer **2** was detrimental to the polymerization of norbornene (**1**). We expected this would lead to *endo*-DCPD being incorporated as a co-monomer with **1** to give random copolymers¹⁰ while also achieving higher molecular weights than seen with **2** alone. Copolymers derived from monomers **1** and **2** were prepared using a feed ratio of monomers (i.e., **1**+**2**) to initiator **4** of

100:1. The polymerizations were run until maximum conversion was reached, which varied based on the relative loading of *endo*-DCPD (**2**). Figure 1 shows good correlation of

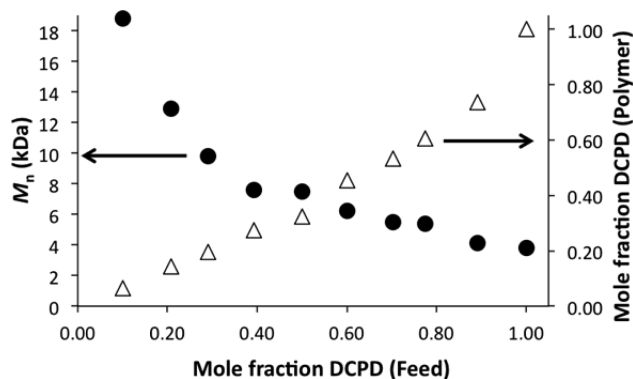


Figure 1. Plot of M_n (●) and DCPD incorporated into final polymer (△) vs DCPD loaded for DCPD/NB copolymerization.

endo-DCPD (**2**) loading to the composition and M_n of the final polymer. Although the amount of **2** incorporated is less than the theoretical amount based upon the feed ratio, the % incorporation shows a consistent increase with increasing initial *endo*-DCPD content. As expected, higher initial loadings of monomer **2** led to a significant decrease in the M_n of the final polymer from 18.8 kDa (~10% DCPD) to 4.1 kDa (~90% DCPD), accompanied by significantly lower conversions and isolated yields. Interestingly, in contrast to the low conversion of **2** at high loadings, small amounts of **2** showed conversions of 50–60%, which suggested to us that decreased reactivity of the monomer was not responsible for low conversions of **2** (see Table S1 in the Supporting Information for full conversion and molecular weight data).

Analysis of the copolymers revealed a linear correlation between DCPD content and glass transition temperature (T_g), as depicted in Figure 2. In each case, we observed a single T_g value, which is consistent with a random polymer microstructure.

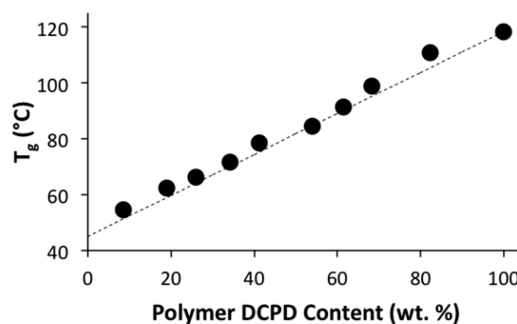


Figure 2. Effect of DCPD content on polymer T_g . The dashed line connects measured values for polynorbornene (45.0 °C) and polydicyclopentadiene (118.3 °C) as measured by DMA.

In an attempt to better understand the reasons for the low conversion, we considered two potential explanations. The first scenario implicates the steric bulk of the additional cyclopentene ring in monomer **2** (compared with **1**), which may impede polymerization. The radical cation likely approaches the monomer's convex face, opposite this cyclopentene ring, making steric interactions in the monomer unlikely as the

reason for the decreased conversion. However, the *endo* orientation results in a ring-opened structure where the propagating chain end is syn to the cyclopentene ring, which may attenuate the rate of new monomer incorporation (Figure 3, top). Alternatively, the additional olefin in the monomer may create problems due to its proximity to the propagating radical cation (Figure 3, middle). The intramolecular reactivity of neighboring olefins with radical cation intermediates is well-documented, and even utilized for the development of cascade reactions.¹¹ While the ultimate fate of these proposed intermediates is unclear, the propensity for *endo*-dicyclopentadiene and related scaffolds to undergo intramolecular reactions of this type¹² or other rearrangements¹³ is well established. Notably, these undesired reactions could arise either during formation of the cyclobutane radical cation (C, Scheme 1) or through the subsequent ring-opened intermediate (E, Scheme 1) during propagation.

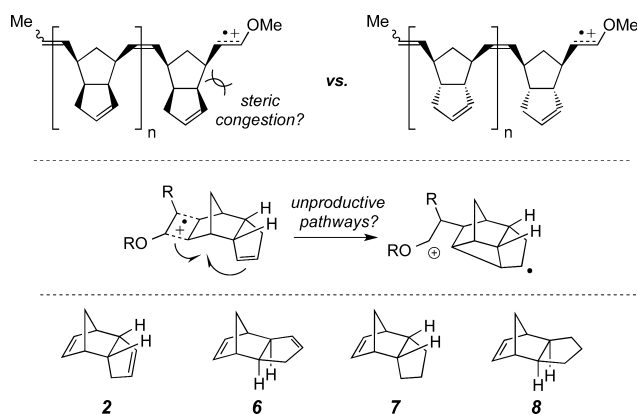


Figure 3. Potential reasons for decreased DCPD conversion and scope of monomers examined.

To probe these two possible pathways, we prepared monomers 6–8 to compare their performance with 2 (Figure 3, bottom). The *exo* configuration of monomer 6 would be expected to perform well if the problem was strictly steric, whereas monomers 7 and 8 avoid the possibility of any undesired intramolecular reactivity with the extra olefin. Previous studies of monomers 2, 6, and 7 using Ru-alkylidene ROMP initiators have found that *exo*-DCPD (6) polymerizes approximately 20 times faster than *endo*-DCPD (2).¹⁴ While this effect is primarily ascribed to steric interactions, coordination of the Ru catalyst by the cyclopentyl olefin does occur to a small extent. In contrast, we believed the poor behavior of 2 under our metal-free conditions was likely due to undesired reactivity of the proposed radical intermediates, given the known proclivity of these species to undergo intramolecular reactions with olefins.^{11,12}

Under our previously reported conditions for photoredox-mediated ROMP, monomers 2, 6, 7, and 8 were each found to undergo polymerization to varying degrees (Figure 4). The *exo*-DCPD monomer (6) was found to perform poorly (approximately 20% conversion, $M_n = 10.8$ kDa; $\bar{D} = 1.4$), similar to what was observed with the *endo* isomer 2. In contrast, the *endo*-dihydroDCPD monomer (7) performed significantly better, typically reaching 50–60% conversion ($M_n = 16.4$ kDa; $\bar{D} = 1.3$). Unfortunately, the resulting polymer displayed poor solubility in dichloromethane, the preferred solvent for polymerization, which may have precluded full

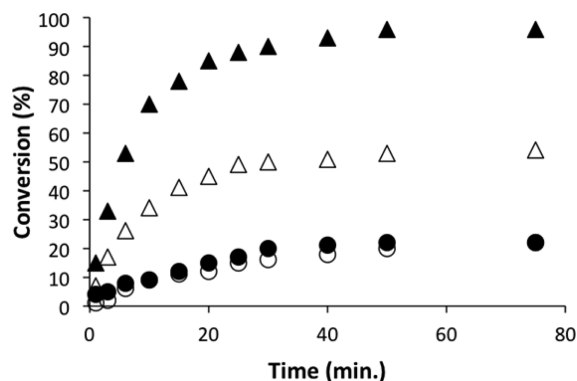


Figure 4. Plot of conversion vs time for monomers 2 (O), 6 (●), 7 (Δ), and 8 (▲) as determined by ¹H NMR spectroscopy.

conversion of monomer.¹⁵ Finally, *exo*-dihydroDCPD (8) performed exceptionally well, reaching >90% conversion ($M_n = 17.2$ kDa, $\bar{D} = 1.3$). This level of conversion is on par with previous studies using norbornene. Taken together, the success of monomers 7 and 8, as well as the poor performance of monomers 2 and 6, suggested to us that the low conversions of the latter monomers are due primarily to the extra unsaturation in the cyclopentene moiety and that steric impedance is not the main culprit. This is in contrast to ROMP utilizing Ru-alkylidene initiators¹⁴ and further highlights the novel mechanism of polymerization.

Based on control experiments, it does not appear that the photoredox-mediated ROMP is intolerant of all olefinic groups. When 1 was polymerized using enol ether 4 in the presence of cyclopentene,¹⁶ a conversion of 79% was observed for norbornene, similar to experiments where cyclopentene is absent. Additionally, no incorporation of cyclopentene was observed by ¹H NMR analysis of the final polymer. Cyclopentene was also found to be unreactive as the sole monomer in polymerizations with initiator 4 or in stoichiometric reactions (see Supporting Information). This provides further support that the conversion-limiting process in the polymerization of 2 and 6 is an intramolecular process. In addition to demonstrating two new monomers that perform well for metal-free ROMP, these studies also provide insight into mechanistic considerations for future monomer design.

The ability to prepare linear polyDCPD is beneficial for the processability of the material and for gaining spatiotemporal control over the onset of cross-linking. Current technologies utilize reaction injection molding, where the monomer and initiator are injected directly into a mold and polymerize to form a molded, cross-linked material.² We explored the possibility of isolating the linear polymer and then carrying out a subsequent reaction to form cross-linked polyDCPD under fully metal-free conditions (Figure 5).¹⁷ We chose to utilize thiol–ene chemistry to achieve the cross-linking due to

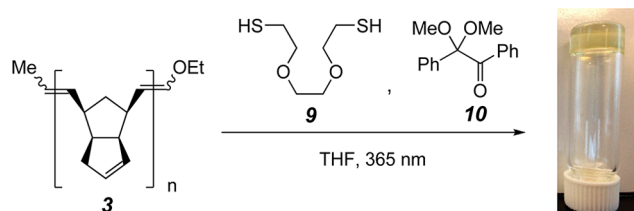


Figure 5. Cross-linking of polyDCPD using a thiol–ene reaction.

the mild conditions, high reactivities, and tunable product properties that have been demonstrated with this approach.^{17c,18} Irradiation of a THF solution of polymer **3** in the presence of dithiol **9** and photoinitiator **10** with a hand-held UV lamp ($\lambda = 365$ nm, 4 W) led to gelation within 30 min (Figure 5).¹⁹ While these cross-linked networks are structurally different from cross-linked polyDCPD prepared using traditional metal-based ROMP initiators, the ability to control the cross-linking temporally while also varying the cross-linking agent is an area of future exploration that may lead to interesting new materials and applications. Future studies will also focus on methods of cross-linking that can be carried out simultaneously with polymerization as well as solvent-free methods which should allow for the preparation of more versatile cross-linked materials using metal-free methods.

In conclusion, we have demonstrated the ability to prepare linear polyDCPD using a photoredox-mediated metal-free ROMP procedure. The monomer, *endo*-DCPD, can also be copolymerized with norbornene to prepare polymers with varied amounts of cyclopentene units. The low conversion observed with this monomer was found to be due to the presence of the additional olefin moiety, and two partially hydrogenated monomers were shown to reach high conversion under the polymerization conditions. Finally, the ability to cross-link the polyDCPD was demonstrated in a manner that avoids metal-based reagents throughout the entire process.

■ ASSOCIATED CONTENT

■ Supporting Information

Detailed experimental procedures, full conversion and molecular weight data for all copolymers, thermal analysis of cross-linked networks, and characterization of all new compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b03665.

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Notes

The authors declare no competing financial interest.

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(16) The ratio of cyclopentene:1:4 = 25:75:1

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(19) Polymers prepared from monomers **1**, **6**, **7**, and **8** also undergo cross-linking under identical conditions.