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Synthesis and Thermo-Selective Recycling of Diels–Alder Cyclopentadiene Thermoplastics

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ABSTRACT: Catalyst-free and reversible step-growth Diels–Alder (DA) polymerization has found a wide range of applications in polymer synthesis and is a promising method to fabricate recyclable thermoplastics. The effectiveness of polymerization and de-polymerization relies on the chemical building blocks, often utilizing furan as the diene and maleimide as the dienophile. Compared to the traditional diene–dienophile or two-component approaches that requires perfect stoichiometry, cyclopentadiene (Cp) can serve a dual role via self-dimerization. This internally balanced platform offers a route to access high-molecular-weight polymers and a dynamic handle for polymer recycling, which remains unexplored. Herein, through the reactivity investigation of different telechelic Cp derivatives, the uncontrolled cross-linking of Cp was addressed, revealing the first successful DA homopolymerization. To demonstrate the generality of our methodology, we synthesized and characterized six Cp homopolymers with backbones derived from common thermoplastics, such as polydimethylsiloxane, hydrogenated polybutadiene, and ethylene phthalate. Among these materials, the hydrogenated polybutadiene–Cp analog can be thermally de-polymerized ($M_n = 68$ to 23 kDa) and re-polymerized to the parent polymer ($M_n = 68$ kDa) under solvent- and catalyst-free conditions. This process was repeated over three cycles without intermediate purification, confirming the efficient thermo-selective recyclability. The varied degradable properties of other four Cp-incorporated thermoplastics were also examined. Overall, this work provides a general methodology to access a new class of reversible homopolymers, potentially expanding the designs and construction of sustainable thermoplastics.

INTRODUCTION

The recognition that macromolecules are formed through the covalent bonding of smaller molecules by Staudinger has led to the discovery of polymers and sparked the industrial fabrication of plastics with applications ranging from packaging and adhesives to modern high-performance materials.^{1,2} Among these materials, linear polymers or thermoplastics have become widely produced and consumed due to their synthetic accessibility and mechanical reprocessability.² Despite a vast array of research efforts, it remains a grand challenge to efficiently recycle these materials and thus, reduce the environmental adverse impact of plastics.^{2–5} One of the most promising strategies to improve polymer sustainability is closed-loop (plastic-to-plastic) chemical recycling.^{6,7} The high-molecular-weight (high-MW) polymers are converted into smaller fragments or intermediates, which are ideally subjected to re-polymerization to form the parent polymer or similarly functional materials. This method is promising to preserve the macromolecular properties and maximize monomer resources.

The current state-of-the-art closed-loop chemical recycling relies on the incorporation of labile bonds into the polymer backbone during the polymer fabrication. This can be accomplished with traditional step-growth polycondensation materials (i.e., polyesters, and polyamides) with the high content of ester or amide groups that are predisposed to well-known chain-breaking conditions.⁸ For example, hydrolysis and glycolysis (through transesterification) of polyethylene terephthalate (PET) have been applied in closed-

loop recycling.^{8–10} The field has also expanded to engineer C–C polymer backbones (e.g., polyolefins, polystyrene, etc.) with hetero-atom-containing units. Under acidic, basic, or metal-catalyzed conditions, the labile bonds are selectively broken, converting the otherwise challenging-to-deconstruct polymers into reusable oligomers or small-molecule starting materials.^{11–15} A variety of chemical strategies have been introduced and optimized to recycle these robust polymers, such as the conventional step-growth esterification,^{11,12} or the favorable chain-growth ring-opening.^{13–15} Other emerging strategies include the exploitation of labile end groups using controlled radical polymerization to efficiently de-polymerize vinyl-based polymers as well as re-polymerize the well-defined chain-end monomer mixtures.^{16–20}

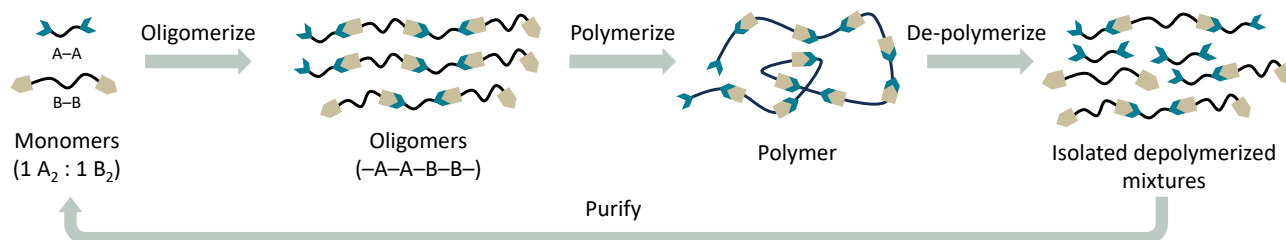
Among the promising closed-loop methodologies, reversible step-growth polymerization (**Figure 1a**) holds the potential to extend the synthetic accessibility, de-polymerization compatibility and thus, optimizing the recycling process. Monomers with discreet chain-ends (i.e., A–A, or B–B) display advantages in terms of finite distances between the degradable units and synthetic accessibility of the functional chain-end building blocks. Moreover, the incorporation of these well-defined chain-ends into “traditional” polymer backbones (e.g., ester, amide, aliphatic, phenyl, carbonate, siloxane, urethane, etc.) provides a straightforward method to enable thermoplastic recycling of commonly used plastics.^{21–23} However, apart from the well-established esterification between carboxylic acids and amines or alcohols, the scope of reversible step-growth methodology

remains underexamined.²³ The prime examples include the ionene formation via a Menshutkin reaction,²⁴ the nucleophilic ring opening reaction (e.g., 2-oxazolin-5-ones and phenol substrates),^{25,26} and the Diels–Alder (DA) [4+2] cycloaddition between furans and maleimides^{27–31} (**Figure 1b**).

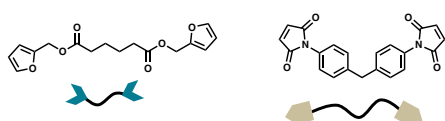
To achieve high-MW polymers, step-growth reactions necessitate monomer purity, quantitative reactivity, and accurate stoichiometry between the A_2 and B_2 monomers.³² These factors are normally difficult to achieve and become particularly challenging when coupled with the design of recyclable polymers. Specifically, it requires a chemical building block that allows efficient forward polymerization yet permits the reverse reaction when triggered. Furthermore,

the strict stoichiometry demands the precise preservation of the de-polymerized chain-ends to successfully reform the parent polymers. Many current methods also rely on chemical reagents (i.e., acids, bases, and catalysts) for de-polymerization and thus, an additional purification step is generally required to access pure A_2 and B_2 monomers to enable closed-loop recycling (**Figure 1a** and **1b**). This adds increased difficulty and cost to re-polymerization strategies and can limit the number of times that the plastics can be recycled. We hypothesize that Diels–Alder step-growth reactions^{31,33} with the prospects of high reactivity and non-chemical stimulus (i.e., heat) for de-polymerization potentially overcomes the challenges associated with additional purification and could increase the number of re-polymerization cycles and generality of closed-loop recycling.

(a) Previous Works – Scheme of Closed-Loop Chemical Recycling Using Two-Component Step-Growth

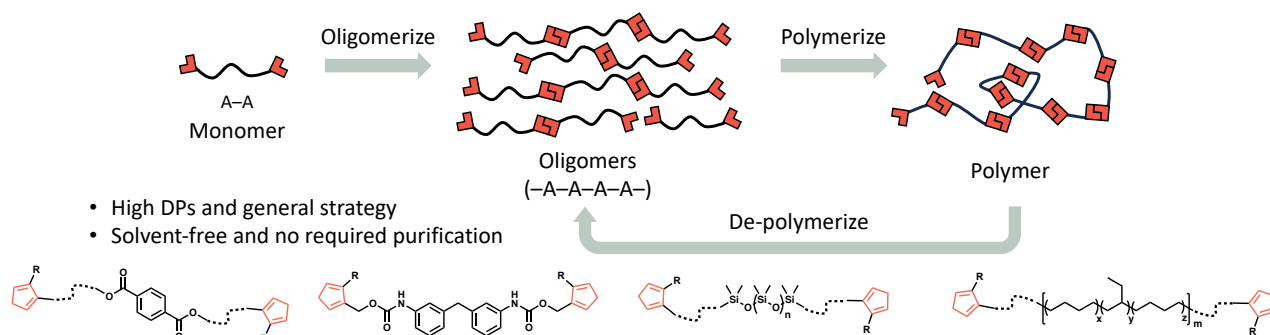


(b) Previous Diels–Alder Reversible Step-Growth: Representative Example of Two-Component System



- Low DPs (< 20) of original polymerization
- Solvent is required in current systems
- Poor re-polymerization due to challenges associated with re-isolation of chain-ends with high purity

(c) This work – Single-Component and Reversible Step-Growth using Diels–Alder Cyclopentadiene Derivatives



- High DPs and general strategy
- Solvent-free and no required purification

Figure 1. (a) General steps that are normally required in a two-component system to chemically recycle step-growth polymers (i.e., $A_2 + B_2$ monomers); the de-polymerization includes the additional purification to achieve high chain-end fidelity of the oligomers/monomers mixture for re-polymerization. (b) The first application of Diels–Alder reaction as reversible step-growth linear polymerization using furan and maleimide materials from Kuramoto and coworkers.⁴³ There remain limitations of furan-maleimide chemistry, involving low degrees of polymerization, poor solubility, and the challenging isolation of pure chain-end monomers/oligomers (c) This work – Cp derivatives for applications in reversible and single-component step-growth polymerization. The internally balanced system is absent of solvents, catalysts, chemical reagents and thus, no isolation is required. The platform also accommodates a variety of common polymer backbones, such as ethylene terephthalate ester, urethane, polydimethylsiloxane (PDMS), and hydrogenated polybutadiene.

The interest in the formation of linear Diels–Alder polymers was initiated by Stille in 1961 via an A_2B_2 -type process using cyclopentadiene (Cp) units as the diene and *p*-benzoquinone or *N,N'*-hexmethylenbismaleimide as the dienophile.³⁴ More than two decades later, Kennedy and Carlson

reported a tenfold chain extension of their functionalized polyisobutylene with terminal silylcyclopentadiene and a bis-maleimide derivative.³⁵ Despite the successful demonstration of these A_2B_2 -type syntheses, there was no follow-up study on this subject, presumably due to the synthetic challenges associated with preparing bis-cyclopentadiene monomers.^{33,36–39} The focus, instead, has been shifted to

furan and maleimide materials after Tesoro and Sastri prepared a bis-furan-functionalized siloxane and initiated polyaddition using a bis-maleimide.⁴⁰ Functionalization of a polymer by furan and maleimide units to obtain the corresponding A_2 and B_2 macromonomers is straightforward and synthetically accessible to a range of polymer backbones.^{27-31,41,42} Unfortunately, the materials generally suffer from poor solubility, slow chain-growth reactivity, and low molecular weights (MWs). Therefore, even though the thermal reversibility of linear furan-maleimide polymers was recognized early by Kuramoto and the coworkers in 1994,⁴³ there still lacks reports about the closed-loop thermo-selective recycling of DA thermoplastics (**Figure 1b**). We hypothesize that overcoming the three main limitations of the current DA tools will provide a pathway to realize the potential of reversible DA step-growth polymerization. First, it is demanding to achieve perfect stoichiometry during both polymerization and recycling process in two-component systems (i.e., A_2B_2 type). Second, the low retro-DA (rDA) temperature (e.g., 110 °C for furan-maleimide adduct) restrains its broad application. Finally, identifying a solvent compatible with both A_2 and B_2 monomers can become problematic, especially during polymer fabrication with a wide range of backbone architectures (**Figure 1b**).

Herein, we propose a unique strategy, utilizing highly reactive cyclopentadiene monomers as single-component and reversible DA monomer units ($A_2 + A_2$, **Figure 1c**). Cp monomers can react with each other due to its high reactivity and dual performance as both diene and dienophile, thereby eliminating the stoichiometry requisite from the two-component or A_2B_2 type process.⁴⁴ Moreover, Cp dimer with a high rDA temperature (i.e., 150–180 °C) potentially broaden the utility of these materials and the accessible MW range. While promising, the synthesis of thermoplastics by Cp homopolymerization has yet to be achieved, primarily because of the absence of accessible synthetic pathways for obtaining pure cyclopentadiene monomers and the challenge of uncontrolled cross-linking with current methods. As a result, the homopolymerization of Cp has been restricted to cross-linked polymers.^{34,36,38,44} Our group previously developed an approach to isolate a pure tetrafunctional cyclopentadiene derivative under mild conditions, allowing us to further understand the polymerizing behavior of Cp in the context of a degradable homopolymer network.⁴⁴ In this study, by investigating different reactivity of bifunctional or telechelic Cp analogs, we have discovered a strategy to enable Cp homopolymerization that leads to high-MW DA linear polymers.

To demonstrate the applicability of our DA recycling platform, we synthesized and characterized a variety of different soluble Cp materials that are integrated with common thermoplastics backbones, such as ethylene terephthalate, urethane, polydimethylsiloxane, and hydrogenated polybutadiene (**Figure 1c**). As planned, the construction and deconstruction of the polymers do not require the presence of catalysts, chemical reagents, and/or solvents. Moreover, as an internally balanced system, no isolation is required to “close the loop.” Multiple re-polymerization cycles are also demonstrated for the hydrogenated polybutadiene-Cp analog. The high-MW polymer can be depolymerized to low-MW oligomers and subsequently re-polymerized to the parent material over the three cycles. This demonstration supports the efficiency of our recycling strategy. Overall, the

methodology involves a general platform for the construction and recycling of DA thermoplastics, potentially expanding access to advanced sustainable polymers.

RESULTS AND DISCUSSION

Synthesis of Cp Derivatives and the Investigation of Subsequent Homopolymerization Efficiency. As shown in our previous report, the sufficient isolation of a pentyl-substituted cyclopentadiene derivative led to the construction of a better-defined network that exhibits tough and elastic properties, opposite to those of prior polymer networks.⁴⁴ To investigate the possible trimer formation, we briefly described the polymerization of a two-arm model Cp monomer. A soluble polymer was formed with the addition of a radical inhibitor, indicating no cross-linking during the step-growth process,⁴⁴ and providing a promising pathway to access high-MW DA linear polymers. Based on the preliminary results, we further investigate the reactivity of multiple bulky Cp analogs to further suppress uncontrolled cross-linking (e.g., trimerization, radical process, etc.), while sustaining the efficient dimerization. The electronic effect of substituents was also explored (i.e., *distal* and *proximal* analogs, based on the relative distance of the carbonyl group to the Cp core). We hypothesized that the realization of these goals will allow us to optimize the synthesis of fully soluble high-MW Cp homopolymers that are potential for efficient thermo-selective recycling (**Figure 2a**).

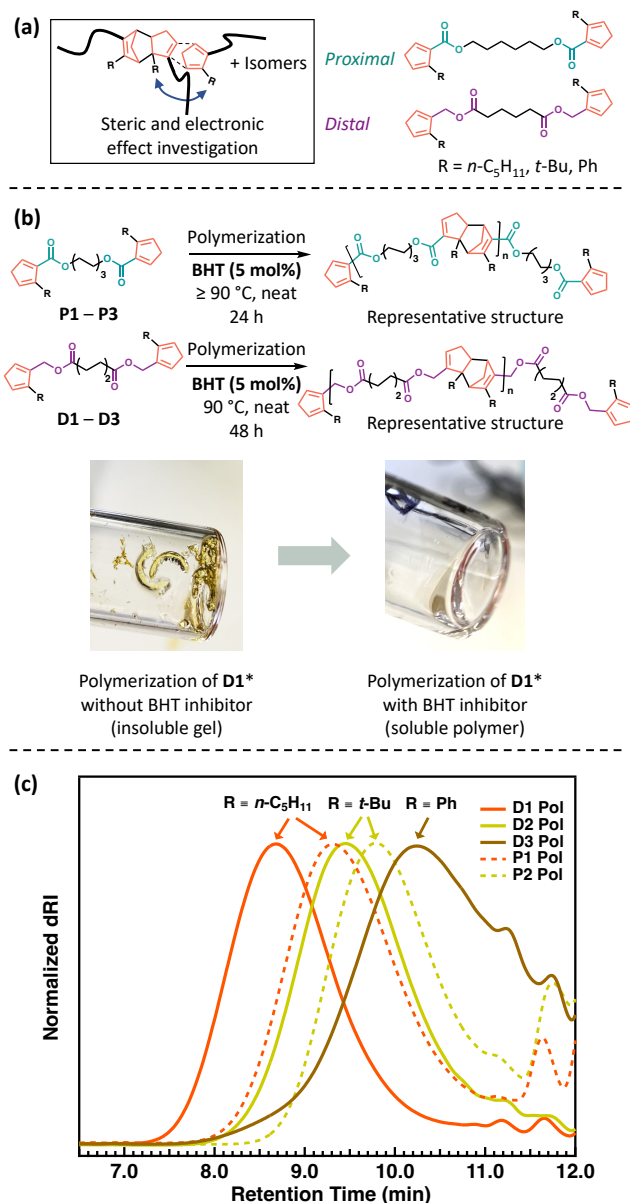


Figure 2. (a) Investigation of different Cp analogs, *distal* versus *proximal* (based on the distance of Cp moiety to the carbonyl functional group), with different substituents (i.e., *n*-pentyl, *t*-butyl, and phenyl) will lead to the optimized synthesis of high-MW Cp linear polymer. The uncontrolled cross-linking process was addressed in this work. (b) The presence of a radical inhibitor, BHT, completely shut down the cross-linking as shown in the bottom pictures. A soluble polymer of **D1** in dichloromethane was observed with the addition of BHT during the polymerization process. *Polymerization conditions: Heating **D1** at 90°C , neat for 24 h. Thus, the screening polymerization of the *proximal* (**P1-P3**) and *distal* (**D1-D3**) analogs was performed with the addition of 5 mol% BHT. (c) The polymerization efficiency of each analog was compared. The *n*-pentyl substituted Cp derivative or **D1** produces the most promising MW range as observed from the SEC traces of **D1**, **D2**, **D3**, **P1** and **P2** polymers with varied substituents ($R = n\text{-C}_5\text{H}_{11}$, $t\text{-Bu}$, and Ph). The optimized polymerization condition is 90°C for 48 h (**D1**, **D2**, and **D3**), 125°C for 22 h (**P1**), and 90°C for 24 h (**P2**).

We utilized the optimized tetrazine-norbornadiene deprotection to prepare and isolate the *proximal* and *distal* Cp analogs.⁴⁴⁻⁴⁶ From a diverse source of alkyne starting

materials (Section 1.3, Supporting Information), six norbornadiene (NBD) precursors were prepared, each with a different substituent attached to the Cp unit to also evaluate the effects of sterics (e.g., *n*-pentyl, *t*-butyl, or phenyl). The ester NBDs **5-7** were prepared on a scale of 5-10 g using alkyne starting materials and dicyclopentadiene (**4**). Analogs **5-7** were then reduced to either alcohol (**8-10**) or converted to the corresponding carboxylic analogs (**14-16**) according to Scheme S1 in Supporting Information. EDC coupling reaction of alcohols **8-10** with adipic acid affords the target *distal* NBD precursors (**11-13**), while the synthesis of *proximal* substrates requires an alternative approach. Both Fischer and Steglich esterification of **14-16** with the alcohols primarily produced the Alder-ene rearranged by-products (Supporting Figure S1, Section 1.4). The same problem occurred with other transesterification methods. Even though Yamaguchi reagents assisted in the formation of the desired product, the conversion was low, and the purification was challenging. Despite these challenges, we discovered that the desired adducts **17-19** could be prepared using a solvent-free nucleophilic substitution ($\text{S}_{\text{N}}2$) reaction. Treatment of 1,6-dibromohexane and the corresponding carboxylic acid with triethylamine (TEA) at 90°C resulted in complete conversion of the desired NBD adducts **17-19** with minimal amount of the rearranged by-product.⁴⁷ Of note, NBD precursors with bulky substituents, **18** and **19** (*t*-butyl and phenyl, respectively) do not undergo rearrangement due to the lack of a hydrogen atom that can participate in the Alder-ene reaction. The synthesized NBD substrates (**11-13** and **17-19**) were then deprotected with 3,6-di-2-pyridyl-1,2,4,5-tetrazine (DpTz) to afford the respective Cp monomers (**D1-D3**, **P1-P3**) (Section 1.3, Supporting Information). As expected, based on our previous work, the *distal* substrates **D1-D3** were efficiently isolated and only one major isomer was observed by ^1H NMR spectroscopy upon isolation. In contrast, accessing pure *proximal* Cp monomers **P1-P3** proved more challenging due to the slow tetrazine deprotection and formation of 1,5-H shift isomeric mixtures. Therefore, *proximal* Cp mixtures were subjected to polymerization without additional purification. Notably, all the above Cp substrates (i.e., **D1-D3** and **P1-P3**) are stored in a freezer (i.e., -20°C) for up to two months to ensure minimal amount of premature dimerization and decomposition of the analogs.

The homopolymerization of each telechelic Cp derivative was performed in different conditions to identify the optimal reaction conditions (Section 1.6, Supporting Information). Initial screening showed gelation of *distal* analogs **D1-D3** immediately after heating at high temperatures, while *proximal* substrates **P1-P3** remained soluble (Supporting Table S1). Contradictory to our hypothesis, the bulkier substituents (*t*-butyl, or phenyl) did not prevent the cross-linking from occurring within the *distal* substrates explored. As for the *proximal* derivatives, despite being soluble, the chain-ends of the formed polymers were not detected by ^1H NMR spectroscopy, even with a short polymerization period. Only mixtures of low MW (< 8 kDa) oligomers were obtained, as characterized by the size exclusion chromatography (SEC) with a polystyrene standard in chloroform solvent (Supporting Table S1). While performing the screening polymerization, we noticed a residual amount of butylated hydroxytoluene (BHT) from dichloromethane (DCM) solvent that was detected on the ^1H NMR spectrum

of the **P1** product. Intriguingly, in the presence of BHT, there was a difference in the polymerization behavior of **P1** (Supporting Figure S58). In the presence of BHT, the end-groups were observed by the ^1H NMR spectroscopy and higher MW was attained. Guided by this observation, we re-investigated the homopolymerization of both the *distal* and *proximal* substrates in the presence of 5 mol% of BHT (**Figure 2b**). Interestingly, despite increase in molecular weights, the polymerization of the *proximal* substrates did not reach the desired range (< 15 kDa), presumably due to the more electron-poor substrates as well as the purification issues as noted above. To our gratification, the radical inhibitor prevented the *distal* analogs from cross-linking and these adducts reached much higher degree of polymerization. Specifically, after polymerizing **D1** at 90°C for 24 h, the material is fully soluble in DCM in the presence of BHT, displaying no cross-linking as observed from the pictures in **Figure 2b**. Within this series, the original pentyl-

substituted Cp (**D1**) monomer showed the highest degree of polymerization (DP_n of 44 and DP_w of 77) among the six analogs (Supporting Table S2 and the SEC spectra from **Figure 2c**). The optimal condition was bulk polymerization of **D1** at 90°C for 48 h, resulting in the highest number-average molecular weight (M_n) of 19.6 kDa and weight-average value (M_w) of 33.9 kDa. In general, the less bulky *distal* Cp derivatives lead to higher-MW polymers. Therefore, we also changed the pentyl group to a less sterically hindered methyl substituent (**22**, Sections 1.3 and 1.6, Supporting Information) to determine if reducing the length of the alkyl chain or sterics will further improve the MW range. Polymerization of **22** results in the similar-MW materials with a higher DP , yet not significant (Supporting Figure S60). Based on the synthetic accessibility and polymerization efficiency, the most promising pentyl-substituted moiety was used to evaluate the generality of the platform with different polymeric backbones.

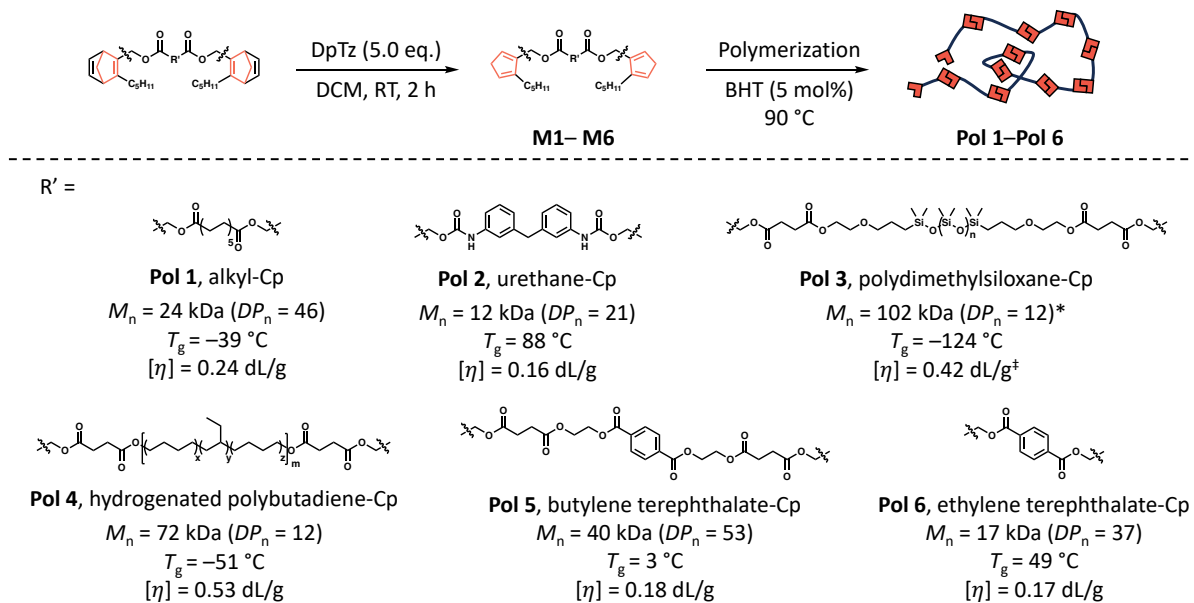


Figure 3. The general scheme to access different Cp monomers (**M1–M6**) via the tetrazine deprotection of varied NBD starting materials. Of note, the pentyl-substituted Cp moiety was incorporated into the common polymer backbones such as alkyl chain (**M1**), urethane (**M2**), polydimethylsiloxane or PDMS (**M3**), hydrogenated polybutadiene (**M4**), butylene terephthalate (**M5**), and ethylene terephthalate (**M6**). The optimized polymerization conditions include the addition of 5 mol% BHT and heating at 90°C in the absence of solvents and stirring, at different time durations. **M1**, **M2**, **M5**, and **M6** need 48 h, while **M3** and **M4** require 96 h to reach the optimized MWs, which are dependent on the backbone flexibility and monomer size. After precipitation to remove BHT, and small oligomers, six pure polymers (**Pol 1–Pol 6**) were acquired and subsequently characterized via an SEC-MALS to delineate the material properties (i.e., accurate number-average molecular weight M_n , glass transition temperature T_g , and intrinsic viscosity $[\eta]$). *Of note, PDMS-Cp analog (**Pol 3**) has an iso-refractive effect with the THF solvent from the instrument, compromising the accuracy of this measurement. †As such, the intrinsic viscosity for **Pol 3** was calculated using a viscometer (Supporting Information 1.12, Table S6, and Figure S93).

Substrate Scope of Cyclopentadiene Homopolymers and Characterization. To demonstrate the versatility of our Cp linear platform, we focused on monomers that are derived from common thermoplastics, including alkyl chain (**M1**), urethane (**M2**), polydimethylsiloxane or PDMS (**M3**), hydrogenated polybutadiene (**M4**), butylene terephthalate (**M5**), and ethylene terephthalate (**M6**) (**Figure 3**). Among these Cp monomers, **M2** is not readily dimerized/polymerized at ambient atmosphere and thus, storing of **M2** at low temperature is not required. The synthesis of polyimide-Cp

polymer was also attempted but only afforded a low-MW polymer ($M_w \approx 8$ kDa) due to the insolubility and hydrolysis-prone issues, as known in literature^{48–50} (Supporting Section 1.8 and Table S3). After purification, the high-MW polymers (**Pol 1–Pol 6**) were characterized by a SEC that is equipped with a triple-detection multi-angle light scattering (MALS) to attain absolute MWs in tetrahydrofuran (THF) solvent (**Figure 3** and Supporting Table S4). Overall, the six polymers possess M_n values ranging from 12 to 102 kDa with the highest DP_n of 53 (**Pol 5**).

To characterize the intrinsic viscosity, Mark-Houwink-Sakurada (MHS) parameters were used.^{51–55} In general,

MHS constant a (Supporting Table S5) indicates expected flexible chains or random coils in THF ($0.5 \leq a \leq 0.8$).⁵¹⁻⁵⁵ The value for PDMS-incorporated Cp polymer (**Pol 3**) was higher than expected ($a = 1.34$), presumably due to the iso-refractive effect with the THF solvent.⁵⁶ The conformation plot (Supporting Figure S79) also shows the same phenomenon, where all the polymer chains, apart from **Pol 3**, possess linear configuration, with low to no degree of branching, as shown by the slope reaching 0.58.⁵⁷ The Cp adducts do not form trimers under the optimized conditions, evident by mass spectrum analysis⁴⁴ and solubility. The intrinsic viscosity and MHS values were analyzed in detail for each polymer analog to probe the solution properties. For urethane-Cp polymer or **Pol 2**, the measured MHS constant a (0.69) is near the value of a similar structure that is reported in literature, or 0.78 in THF.⁵⁸ **Pol 1** and **Pol 4** have the solution properties similar to the saturated hydrocarbon polymer, especially polyisobutylene.⁵⁹ Due to iso-refractive effect of THF with **Pol 3**, a viscometer was utilized to measure the polymer behavior in toluene (Supporting Section 1.12, Table S6 and Figure S93). The intrinsic viscosity was determined to be 0.42 dL/g (from both Huggins and Kraemer plots) for $M_w \approx 102$ kDa, matching the literature trend for the same MW range.⁶⁰ Both **Pol 5** and **Pol 6** display lower intrinsic viscosity in THF compared to the literature values of commercial polybutylene terephthalate (PBT) and polyethylene terephthalate (PET), respectively, in other solvents (e.g., *m*-cresol, *o*-chlorophenol).^{61,62} When solvents are not present in the intrinsic viscosity measurement via the infrared spectroscopy and multivariate calibration method, the value of **Pol 6** is close to that of the post-consumer PET.⁶³

We also conducted thermal characterization to probe material properties. Each Cp polymer displays a range of different glass transition temperature (T_g) that was measured via a differential scanning calorimetry (DSC) (**Figure 3**). PDMS-Cp polymer (**Pol 3**) exhibits the lowest T_g of -124 °C, while PU-derived analog (**Pol 2**) provides the highest T_g of 88 °C. These results aligned with literature reports.⁶⁴ The dodecane ester Cp polymer (**Pol 1**) has a reasonably similar T_g range with its hydrogenated butadiene counterpart (**Pol 4**). The butylene phthalate-Cp polymer (**Pol 5**) has a lower T_g of 3 °C, compared to commercial PBT, which is $27-60$ °C.⁶⁴ **Pol 6** has a reasonably higher T_g of 49 °C than **Pol 5** due to the shorter alkyl chain. However, it is still lower than the known value. One of the reasons can be related to the lower M_w of **Pol 6** compared with that of the commercial PET ($M_w \geq 30,000$ Da).⁶⁴ In general, however, the T_g of the DA-linked thermoplastics were comparable with known commercial analogs.

To extend the property studies of these materials, **Pol 6** was chosen for mechanical evaluation. The glassy nature and ease of melt processing of **Pol 6** made it an accessible candidate for the mechanical analysis. We performed tensile testing on **Pol 6** using both crude and purified materials, which were melted into the dumbbell-shaped samples (more details in Supporting Section 1.13). The ultimate tensile strength is measured to be $18-22$ MPa with $\sim 5-7\%$ elongation and the Young's modulus value of ~ 500 MPa (Supporting Figures S94-95, and Table S7). We also performed the test on a sample derived from crude material using the American Society for Testing and Materials (ASTM) D638-14 standard⁶⁵ (Supporting Figures S96 and S97),

which has tensile strength of 15 MPa, elongation at break of 2% , and Young's modulus of 1.2 GPa. The performance of **Pol 6** is comparable with the studies of virgin and recycled PET fibers,⁶⁶ but lower than that of the commercial PET resin.⁶⁴ Of note, melt processing under ambient atmosphere was applied to mold the samples (~ 90 °C) multiple times before the mechanical characterization. This could potentially affect the original mechanical properties due to the inevitable thermal degradation of PET during the melt processing.⁶⁷

Investigation of Active Chain-Ends and Optimal MW Range. To potentially control and increase the MW range for varied applications, we investigated the Diels-Alder polymerizing behaviors of Cp. First, active chain-ends were probed by reacting **Pol 1** ($M_n = 24$ kDa) with N15-labeled phenyl maleimide (¹⁵N-PhMal) at room temperature with DCM as the solvent. To our surprise, no signal was detected for the Cp-maleimide adduct based on the ¹H-¹⁵N heteronuclear multiple bond correlation (HMBC) NMR spectrum. Factors that could affect the end-group reactivity with maleimide include the formation of cyclic polymers, decomposition of the functional Cp units, and/or the polymers have reached the chemical equilibrium. To inspect chain-end cyclization, we heated **Pol 1** at 150 °C for 2 min in the presence of ¹⁵N-PhMal "capping" reagent. As known in the field, the physically more compact circular polymers occupy smaller hydrodynamic volumes and thus, exhibit lower-MW reading on the SEC spectra than the linear analogs.⁶⁸ We hypothesize that after short thermal de-polymerization, the "hypothetically cyclic" Cp polymer would change to a linear conformation, leading to an SEC trace at higher-MW region. However, due to the incorporation of Cp units across the polymer backbone, **Pol 1** also starts to de-polymerize at 150 °C even during a short amount of time (i.e., 2 min) to smaller fragments and displayed an overall lower-MW reading on the SEC spectrum (Supporting Section 1.14). As such, we were only able to confirm the formation of reactive Cp units after a brief de-polymerization at 150 °C (Supporting Figures S98 and S101). Given this challenge, we also monitored the polymerization process and tracked the chain-ends via ¹H NMR spectroscopy. A predictable step-growth polymerizing mechanism with approximately $95-98\%$ conversion was observed (**Figure 4**), based on the consumption of Cp and M_n values (Supporting Table S8 and Section 1.14).

To investigate the possible decomposition of functional Cp chain-ends, the amount of BHT was increased to 10 mol% but there was no further chain extension, while lowering the amount to less than 1 mol% showed gradual degradation/oxidation of the macromolecule (Supporting Figure S103). Different inhibitors (e.g., hydroquinone and mequinol) were also investigated to observe their effect to the polymerization but no improvement was observed (Supporting Figure S104). Of the inhibitors examined, BHT was shown to prevent the degradation of Cp materials the most effectively and result in the optimal MW. The polyaddition could also be haunted due to other reasons than decomposition, such as reaching a thermodynamic equilibrium, ceiling temperature,⁶⁹ or limitations caused by the bulk polymerization (e.g, diffusion-controlled reaction, improper heat transfer, etc.).^{70,71} The kinetics of the step-growth reaction of Cp dimerization could also potentially affect the $DP^{33,51}$ and influence the polymerizing behaviors.

To test if higher MW could be achieved by increasing the reaction rate of the system, two-component Cp-maleimide polymerization was also attempted (Supporting Figure S105). However, this did not result in higher MW despite the faster kinetics of Cp and maleimide as known in literature.^{39,45,46,72-75}

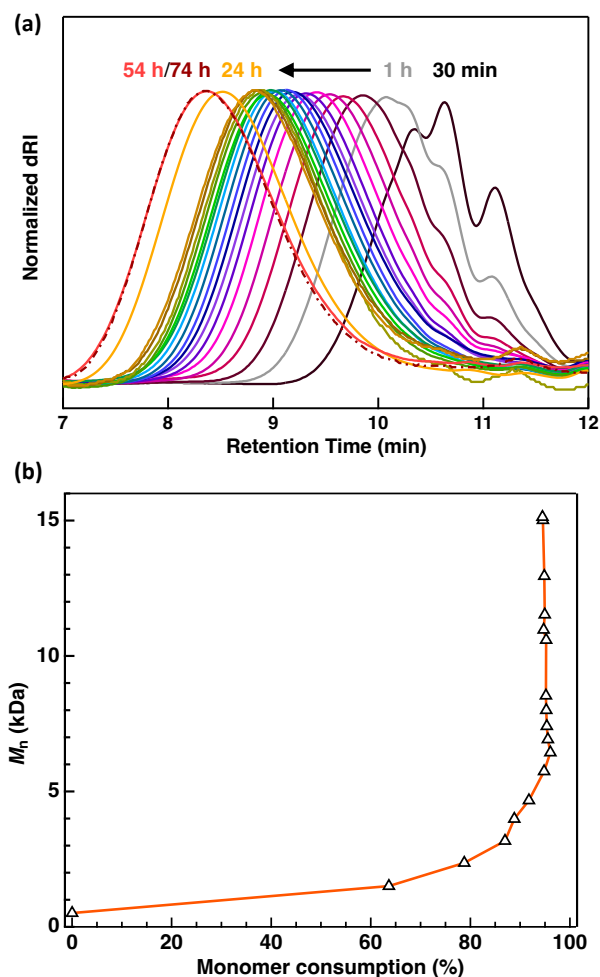


Figure 4. (a) The polymerization of **M1** (with 5 mol% BHT) at 90 °C was monitored throughout the course of 74 h with the SEC traces recorded at 30-min intervals between 0.5 and 8 h, and then at 24, 54, and 74 h. The highest MW was obtained at 54 h. (b) The monomer consumption from ¹H NMR spectra were coupled with M_n values to determine the polymerization kinetics. In the first 30 min, more than 60% monomer was consumed. A step-growth mechanism is revealed as expected from the Diels–Alder linear polymerization with a conversion of approximately 95–98%.

Thermo-Selective Recycling of Cp Homopolymers. To demonstrate the reversible DA design, selected homopolymers were subjected to recycling experiments by first de-polymerization at 150 °C (the onset of rDA temperature range) and re-polymerization at 90 °C in the same pot without solvent and purification throughout the closed-loop process. All materials were characterized via the standard chloroform SEC. Specifically, hydrogenated polybutadiene that is integrated with Cp dimers or **Pol 4** ($M_n = 68$ kDa, DP_n of 11) was heated at 150 °C, neat (in the presence of 1 wt% BHT) and the de-polymerization was monitored at 5, 15, and 30 min (**Figure 5a**). **Pol 4** reverted to smaller oligomers within 5 min. Heating the material longer, 15 min and

30 min, provided shorter polymer chains (**Figure 5a**). However, no further change in molecular weight was observed after 30 min of heating (Supporting Figure S110). Under these conditions, the de-polymerized material was determined to possess M_n of 23 kDa (DP_n of ~4, contributing to ~70% de-polymerization efficiency). The re-polymerization was achieved by heating the lowest-MW oligomers (23 kDa, dotted-green SEC trace from the graph in **Figure 5a**) at 90 °C, neat for 96 h, following the original optimal polymerization conditions for **Pol 4**. The MW was fully recovered to that of the parent polymer (dark purple SEC trace). The closed-loop process was repeated over 3 cycles and the near-identical results were observed (**Figure 5a** and **5b**).

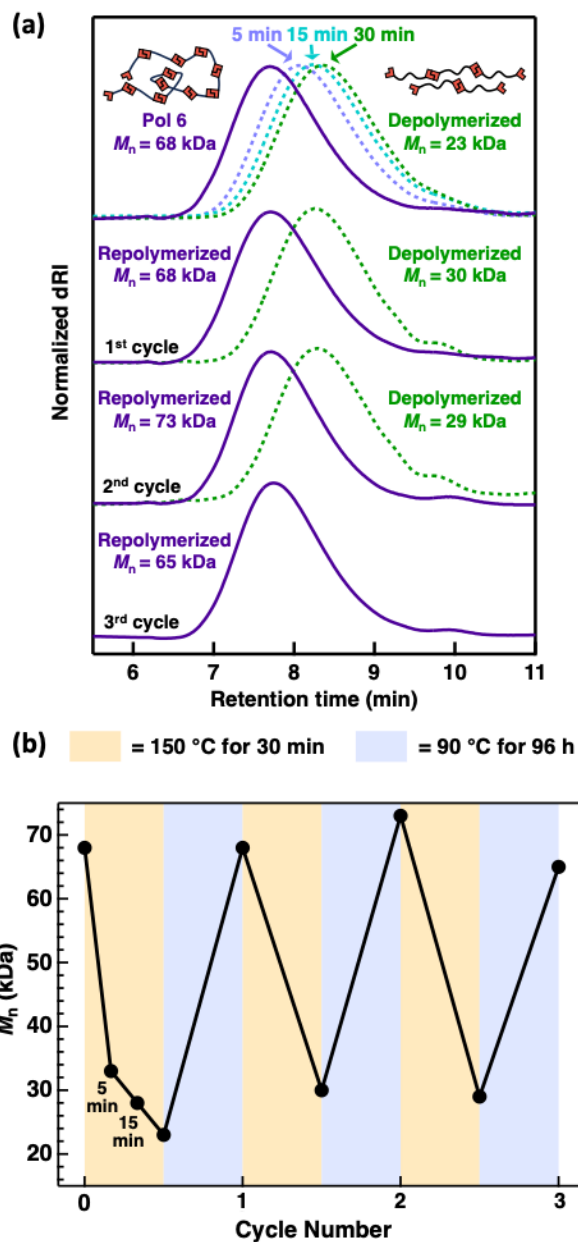


Figure 5. (a) Hydrogenated polybutadiene that is integrated with Cp dimers (**Pol 4**) was subjected to 3 cycles of de- and re-polymerization processes with the addition of 1 wt% BHT, in the absence of solvents. The first cycle involves the heating of **Pol 4** ($M_n = 68$ kDa) at 150 °C for 5, 15, and 30 min (top SEC traces). **Pol 4** was efficiently de-polymerized ($M_n = 68$ kDa to

23 kDa) after 30 min. No purification was performed as the resulting oligomer ($M_n = 23$ kDa) was directly subjected to the re-polymerization (i.e., 90 °C for 96 h). A full recovery to the original MW was observed (middle SEC traces). The process was repeated two more times (middle and bottom SEC traces). The phenomenon persisted with consistent de- and re-polymerization patterns. (b) Thermal reversibility of **Pol 4** is highly efficient and can be recycled multiple times (i.e., 3 cycles), displaying the potential of single-component step-growth.

The de- and re-polymerization of **Pol 1**, **Pol 2**, **Pol 3**, and **Pol 6** were also performed with the same conditions as shown for **Pol 4**. Diverse behaviors were attained among the materials (Supporting Information, Section 1.16). Specifically, **Pol 2** was successfully de-polymerized to the oligomers with M_n of 5 kDa, which was subsequently re-polymerized. The recovered material displays a higher-MW range compared to the original polymer (Supporting Information, Figure S114). **Pol 1** and **Pol 6** successfully degraded upon heating but unexpectedly did not show efficient re-polymerization behaviors, regardless of the varied de- and re-polymerization conditions (e.g., change in the amount of BHT, purification of de-polymerized mixtures, re-polymerization with different solvents and temperatures; more details are described in Supporting Information, Section 1.16). Of note, these polymers contain higher concentration of Cp linkages as well as ester linkages (i.e., Cp dimer and ester units are distributed per ~ 0.5 kDa along the polymer backbone), which could contribute to thermal degradation and insufficient re-polymerization.⁷⁶ As aforementioned, critical purity of oligomer chain-ends is required to achieve the reformation of the parent polymers. Therefore, minimal degradation of Cp chain-ends or ester linkages can have detrimental effects on the re-polymerization. When **Pol 6** was heated for a shorter amount of time (15 min rather than 30 min), the re-polymerization is slightly improved (Supporting Figure S119), supporting our degradation hypothesis. Furthermore, the color of **Pol 6** was changed from transparent to light yellowish during the heating process, showing the partial degradation of the polymer (Supporting Figure S120). The siloxane-Cp analog, or **Pol 3**, which was polymerized from a macromolecular monomer and thus, contain lower concentration of Cp and ester moieties (i.e., per 7–11 kDa along the polymer backbone), displays the closest trait to that of **Pol 4**. The original MW was recovered and close to that of the original polymer (Supporting Information, Figure S122). ¹H NMR spectra of the de-polymerized materials were also collected for **Pol 1–4** and **Pol 6**, which reveal the Cp chain-ends (Supporting Figures S113, S115, S117, S121, and S123). In this work, only recycling of homopolymer was demonstrated, nevertheless, up-recycling with different functionalized dienophiles is feasible and under ongoing investigation.

CONCLUSIONS

We have demonstrated a new and straightforward methodology to form high-MW recyclable thermoplastics, utilizing single-component cyclopentadiene derivatives and the Diels–Alder polymerization/de-polymerization. In this initial study, we synthesized and characterized six Cp homopolymers that are based on common thermoplastics architectures. All tailored materials possess an excellent range of material properties (e.g., varied glass transition temperatures, flexible backbones, etc.) and show consistent de-

polymerization behaviors, except for the substances that contain high amount of Cp and ester linkages. Here, the unavoidable thermal degradation presumably contributed to the complication during the re-polymerization process. Remarkably, the hydrogenated polybutadiene that is modified with Cp units (**Pol 4**) displays the ability to efficiently re-polymerize and de-polymerize over three cycles. Moreover, due to the single-component DA chemistry, no catalysts, or solvents and thus, no purification step is required during the recycling process. Overall, synthesis and characterization of the recyclable Cp homopolymers presents insights into the similar and different properties, compared to the current state-of-the-art thermoplastics, consequently creating a space for further improvement and additional analysis. Specifically, in-dept structure-property relationship studies are important to improve the MW range of the synthesized polymer, to prevent degradation during recycling, or to understand the spatial arrangements of Cp-dimer that affect the material properties. We believe this work could establish a mild and universal thermo-selective recycling strategy that expands the design and construction of sustainable thermoplastics. Furthermore, in the realm of mixed plastics, polymers modified with Cp dimer units can be thermo-selectively depolymerized in the presence of other traditional polymers. Assuming the reactive Cp chain-ends after de-polymerization, the re-polymerization of a mixture of drastically different polymers to form new types of recycled materials can also be realized.

ASSOCIATED CONTENT

Supporting Information

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Synthetic procedures, characterization (NMR, FTIR, mass spectrometry, SEC, SEC-MALS, TGA, DSC, and viscometer), mechanical testing via Texture Analyzer, and detailed chemical recycling results (PDF).

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Author Contributions

TMT performed all the above experiments and data analyses. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

Authors declare that they have no competing interests.

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ABBREVIATIONS

MW, molecular weight; DA, Diels–Alder; rDA, retro-Diels–Alder; Cp, cyclopentadiene; NBD, norbornadiene; DpTz, 3,6-di-2-pyridyl-1,2,4,5-tetrazine; TEA, triethylamine; BHT, butylated hydroxytoluene; SEC, size exclusion chromatography; MALS, multiple-angle light scattering; DCM, dichloromethane; THF, tetrahydrofuran; MHS, Mark-Houwink-Sakurada; HMBC, heteronuclear multiple bond correlation; PBT, polybutylene terephthalate; PET, polyethylene terephthalate; PDMS, polydimethylsiloxane; NMR, nuclear magnetic resonance.

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