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

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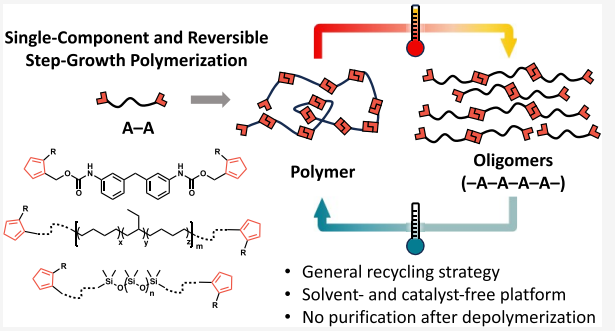
ABSTRACT: Catalyst-free and reversible step-growth Diels–Alder (DA) polymerization has a wide range of applications in polymer synthesis and is a promising method for fabricating recyclable thermoplastics. The effectiveness of polymerization and depolymerization relies on the chemical building blocks, often utilizing furan as the diene and maleimide as the dienophile. Compared to the traditional diene–dienophile or two-component approach that requires precise stoichiometry, cyclopentadiene (Cp) can serve dual roles via self-dimerization. This internally balanced platform offers a route to access high-molecular-weight polymers and a dynamic handle for polymer recycling, which has yet to be explored. Herein, through a 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 poly(dimethylsiloxane), hydrogenated polybutadiene, and ethylene phthalate. Among these materials, the hydrogenated polybutadiene-Cp analog can be thermally depolymerized (M_n = 68 to 23 kDa) and repolymerized 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 the other four Cp-incorporated thermoplastics were also examined. Overall, this work provides a general methodology for accessing a new class of reversible homopolymers, potentially expanding the design 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] High-molecular-weight (high-MW) polymers are converted into smaller fragments or intermediates, which are ideally subjected to repolymerization to form the parent polymer or similarly functional materials. This method is promising for preserving macromolecular properties and maximizing monomer resources.

The current state-of-the-art closed-loop chemical recycling relies on the incorporation of labile bonds into the polymer backbone during polymer fabrication. This can be accomplished with traditional step-growth polycondensation materials (i.e., polyesters and polyamides) using high ester or amide content 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 heteroatom-containing units. Under acidic, basic, or metal-catalyzed conditions, the labile bonds are selectively broken, converting 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 conventional step-growth esterification,[11,12] or favorable chain-growth ring opening.[13−15] Other emerging strategies include the exploitation of labile end groups using controlled radical polymerization to efficiently

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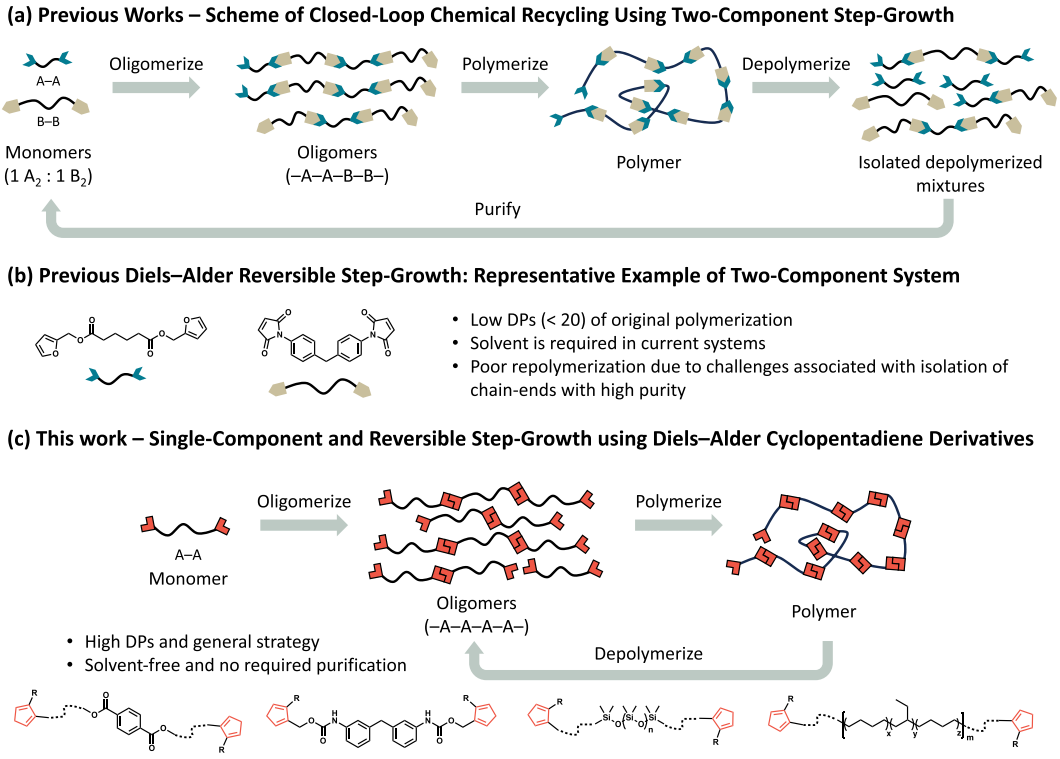

Figure 1. (a) General steps that are normally required in a two-component system to chemically recycle step-growth polymers (i.e., A_2 + B_2 monomers); the depolymerization includes additional purification to achieve high chain-end fidelity of the oligomers/monomers mixture for repolymerization. (b) The first application of the Diels−Alder reaction as reversible step-growth linear polymerization using furan and maleimide materials from Kuramoto and co-workers.[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 presents Cp derivatives for applications in reversible and single-component step-growth polymerization. An internally balanced system is lacking of solvents, catalysts, and chemical reagents; thus, no isolation is required. The platform also accommodates a variety of common polymer backbones, such as ethylene terephthalate, urethane, poly(dimethylsiloxane) (PDMS), and hydrogenated polybutadiene.

depolymerize vinyl-based polymers as well as repolymerize the well-defined chain-end monomer mixtures.[16−20]

Among the promising closed-loop methodologies, reversible step-growth polymerization (Figure 1a) has the potential to extend the synthetic accessibility and depolymerization compatibility, thus, optimizing the recycling process. Monomers with discrete chain ends (i.e., A−A or B−B) display advantages in terms of the 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 the reversible step-growth methodology remains underexamined.[23] The prime examples include ionene formation via a Menshutkin reaction,[24] the nucleophilic ring-opening reaction (e.g., 2-oxazolin-5-ones and phenol substrates),[25,26] and 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 A_2 and B_2 monomers.[32] These factors are normally difficult to achieve and are particularly challenging when coupled with the design of recyclable polymers. Specifically, it requires a chemical building block that allows efficient forward polymerization yet permittting the reverse reaction when triggered. Furthermore, the strict stoichiometry demands the precise preservation of the depolymerized chain ends to successfully reform the parent polymers. Many current methods also rely on chemical reagents (i.e., acids, bases, and catalysts) for depolymerization; thus, an additional purification step is generally required to access pure A_2 and B_2 monomers to enable closed-loop recycling (Figure 1a,b). This increases the difficulty and cost of repolymerization strategies and can limit the number of times that plastics can be recycled. We hypothesized that DA step-growth reactions[31,33] with the prospects of high reactivity and nonchemical stimulus (i.e., heat) for depolymerization potentially overcome the challenges associated with additional purification and could increase the number of repolymerization cycles and generality of closed-loop recycling.

The interest in the formation of linear DA polymers was initiated by Stille in 1961 via an A_2B_2-type process using cyclopentadiene (Cp) derivatives as diene and *p*-benzoquinone or *N,N′*-hexmethylenebismaleimide as the dienophile.[34] More than two decades later, Kennedy and Carlson reported a 10-fold 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

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materials after Tesoro and Sastri prepared a bis-furan-functionalized siloxane and initiated polyaddition using a bis-maleimide.[40] The 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, 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 co-workers 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 current DA tools can provide a pathway to realize the potential of reversible DA step-growth polymerization. First, it is demanding to achieve precise stoichiometry during both the polymerization and recycling processes 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 be 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 their high reactivity and dual performance as both dienes and dienophiles, thereby eliminating the stoichiometric requisite from the two-component or A_2B_2-type process.[44] Moreover, Cp dimers with a high rDA temperature (i.e., 150−180 °C) potentially broadened the utility of these materials and enabled their 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 using the current methods. As a result, the homopolymerization of Cp is restricted to cross-linked polymers.[34,36,38,44] Our group previously developed an approach for isolating 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 reactivities of bifunctional or telechelic Cp analogs, we 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 integrated with common thermoplastic backbones, such as ethylene terephthalate, urethane, poly(dimethylsiloxane), and hydrogenated polybutadiene (Figure 1c). As planned, the construction and deconstruction of 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 repolymerization cycles are also demonstrated for the hydrogenated polybutadiene-Cp analog. The high-MW polymer was depolymerized to low-MW oligomers and subsequently repolymerized to the parent material over 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 exhibited tough and elastic properties, unlike those of prior polymer networks.[44] To investigate the possible trimer formation, we briefly describe the polymerization of a two-arm Cp monomer. A soluble polymer was formed with the addition of a radical inhibitor, indicating that no cross-linking occured during the step-growth process,[44] and thus provide a promising pathway for accessing high-MW DA linear polymers. Based on the preliminary results, we further investigated 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 effects of substituents were 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 with potential for efficient thermo-selective recycling (Figure 2a).

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), 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. The 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 alcohols primarily produced the Alder-ene rearranged byproducts (Section 1.4). The same problem occurred with the other transesterification methods. Even though Yamaguchi reagents assisted in the formation of the desired product, the conversion rate 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 (S_N2) 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 byproduct.[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 hydrogen atoms 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). As expected, based on our previous work, the *distal* substrates **D1**−**D3** were efficiently isolated and only one major isomer was observed by ^{1}H NMR spectroscopy upon isolation. In contrast, accessing pure *proximal* Cp monomers **P1**−**P3** was more challenging due to slow tetrazine

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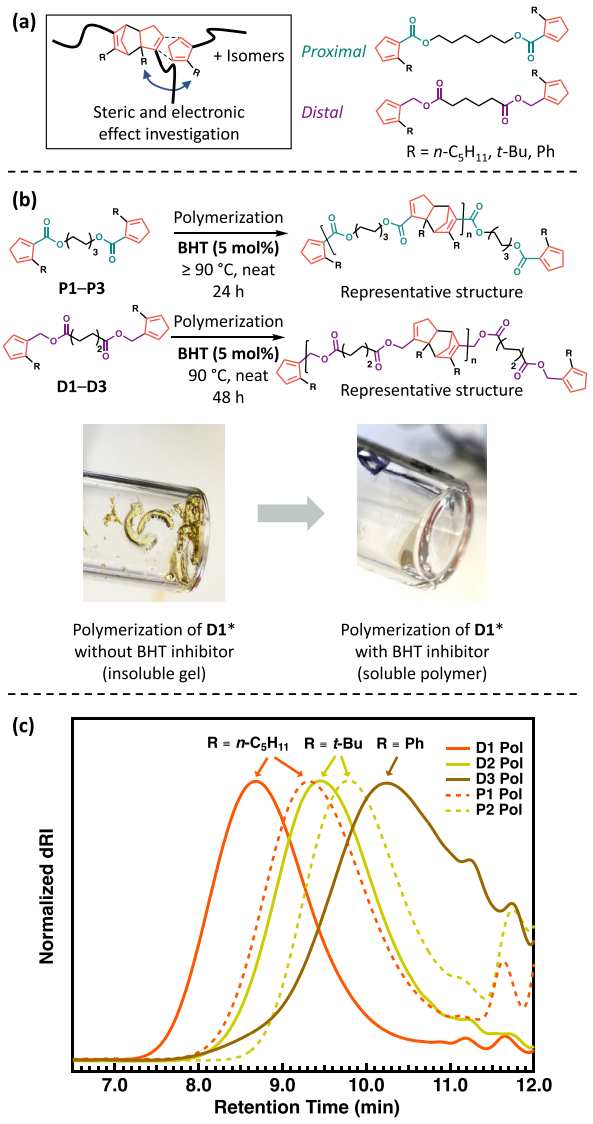

Figure 2. (a) Investigation of different Cp analogs, *distal* versus *proximal* (based on the distance of Cp moiety to the carbonyl functional group), with different substituents (i.e., *n*-pentyl, *t*-butyl, and phenyl) will lead to the optimized synthesis of the high-MW Cp linear polymer. The uncontrolled cross-linking process was addressed in this work. (b) The presence of a radical inhibitor, BHT, completely inhibited the cross-linking, as shown in the bottom pictures. A soluble polymer of D1 in dichloromethane was observed upon the addition of BHT during the polymerization process. Thus, the screening polymerization of the *proximal* (**P1**−**P3**) and *distal* (**D1**−**D3**) analogs was performed with the addition of 5 mol % BHT. *Polymerization conditions of **D1**: heating **D1** at 90 °C for 24 h (no stirring and solvents). (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-C_5H_{11}, *t*-Bu, and Ph). The optimized polymerization conditions are 90 °C for 48 h (**D1**, **D2**, and **D3**), 125 °C for 22 h (**P1**), and 90 °C for 24 h (**P2**).

deprotection and formation of 1,5-hydrogen shift isomeric mixtures. Therefore, the *proximal* Cp mixtures were subjected to polymerization without additional purification. Notably, all the above Cp substrates (i.e., **D1**−**D3** and **P1**−**P3**) were stored in a freezer (i.e., − 20 °C) for up to two months to ensure minimal premature dimerization and decomposition of the analogs.

The homopolymerization of each telechelic Cp derivative was performed under different conditions to identify the optimal reaction conditions (Section 1.6). 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). Contrary to our hypothesis, bulkier substituents (*t*-butyl or phenyl) did not prevent cross-linking within the *distal* substrates explored. Regarding the *proximal* derivatives, despite being soluble, the chain ends of the formed polymers were not detected by ^{1}H NMR spectroscopy, even with a short polymerization period. Only mixtures of low MW (<8 kDa) oligomers were obtained, as characterized by 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, which was detected in the ^{1}H 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 ^{1}H NMR spectroscopy, and a higher MW was attained. Based on this observation, we reinvestigated the homopolymerization of both the *distal* and *proximal* substrates in the presence of 5 mol % BHT (Figure 2b). Interestingly, despite the 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 noted above. To our knowledge, the radical inhibitor prevented the *distal* analogs from cross-linking, and these adducts reached a much higher degree of polymerization. Specifically, after polymerizing **D1** at 90 °C for 24 h, the material was fully soluble in DCM in the presence of BHT, and no cross-linking was displayed, as observed from the 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 the 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 a 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) to determine whether reducing the length of the alkyl chain or sterics will further improve the MW range. Polymerization of **22** results in similar-MW materials with a higher *DP*, yet it is 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.

Substrate Scope of Cyclopentadiene Homopolymers and Characterization. To demonstrate the versatility of our Cp linear platform, we focused on monomers derived from common thermoplastics, including alkyl chains (**M1**), urethane (**M2**), poly(dimethylsiloxane) 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 temperature; thus, storing of **M2** at low temperatures

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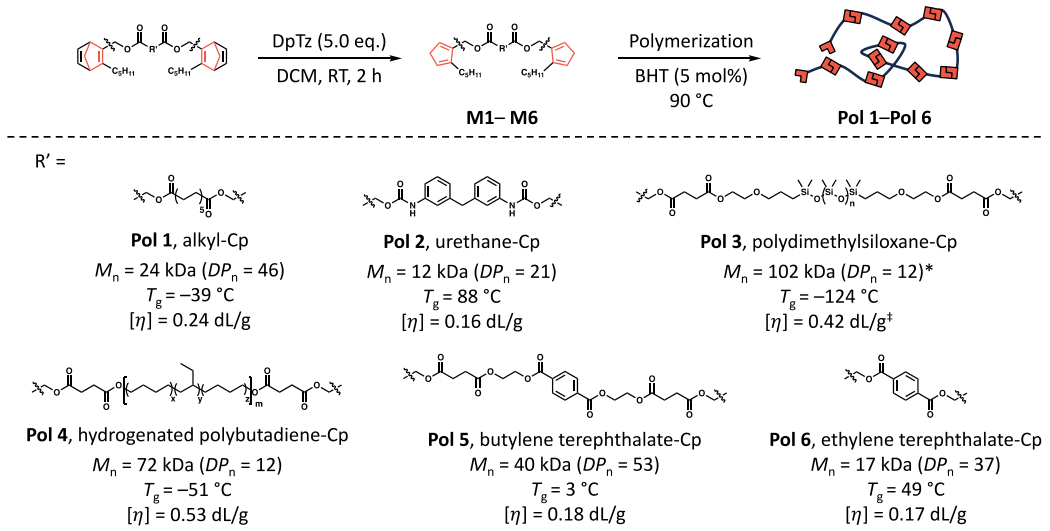

Figure 3. General scheme to access different Cp monomers (**M1**–**M6**) via the tetrazine deprotection of varied NBD starting materials. Of note, the pentyl-substituted Cp moiety was incorporated into the common polymer backbones, such as alkyl chains (**M1**), urethane (**M2**), poly(dimethylsiloxane) or PDMS (**M3**), hydrogenated polybutadiene (**M4**), butylene terephthalate (**M5**), and ethylene terephthalate (**M6**). The optimized polymerization conditions included the addition of 5 mol % BHT and heating at 90 °C in the absence of solvents and stirring for different time durations. **M1**, **M2**, **M5**, and **M6** required 48 h, while **M3** and **M4** required 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 SEC-MALS to delineate the material properties (i.e., accurate number-average molecular weight M_n, glass transition temperature T_g, and intrinsic viscosity [η]). *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).

is not required. The synthesis of the polyimide-Cp polymer was also attempted but only afforded a low-MW polymer (M_w ≈ 8 kDa) due to the insolubility and hydrolysis-prone issues reported 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 equipped with a triple-detection multiangle 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, the MHS constant a (Supporting Table S5) indicates the expected flexible chains or random coils in THF ($0.5 \leq a \leq 0.8$).[51−55] The value for the 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 a 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 analysis[44] 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 reported in the literature, or 0.78 in THF.[58] **Pol 1** and **Pol 4** have solution properties similar to the saturated hydrocarbon polymer, especially polyisobutylene.[59] Due to the 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 ≈ 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 PET, respectively, in other solvents (e.g., *m*-cresol, *o*-chlorophenol).[61,62] When solvents are not present in the intrinsic viscosity measurement via infrared spectroscopy and multivariate calibration method, the value of **Pol 6** is close to that of postconsumer PET.[63]

We also conducted thermal characterization to probe the material properties. Each Cp polymer displays a range of different glass transition temperature (T_g) that was measured via differential scanning calorimetry (DSC) (Figure 3). PDMS-Cp polymer (**Pol 3**) exhibits the lowest T_g of −124 °C, while the 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 than commercial PBT, which is 27–60 °C.[64] **Pol 6** has a reasonably higher T_g of 49 °C than **Pol 5** due to its 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 was comparable with those of 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** make it an accessible candidate for mechanical analysis. We performed tensile testing on **Pol 6** using both crude and purified materials, which were melted into dumbbell-shaped samples (more details in Supporting Section 1.13). The ultimate tensile strength was measured to be 18–22 MPa with ∼5–7% elongation and a Young's

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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 standard[65] (Supporting Figures S96 and S97), which has a 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 those of the virgin and recycled PET fibers,[66] but lower than that of 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 can potentially affect the original mechanical properties due to the inevitable thermal degradation of PET during 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 DA polymerization behaviors of Cp. First, active chain ends were probed by reacting **Pol 1** (M_n = 24 kDa) with N15-labeled phenyl maleimide (^{15}N-PhMal) at room temperature with DCM as the solvent. To our surprise, no signal was detected for the Cp-maleimide adduct based on the ^{1}H-^{15}N 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, or the polymers reaching the chemical equilibrium. To investigate chain-end cyclization, we heated **Pol 1** at 150 °C for 2 min in the presence of the ^{15}N-PhMal "capping" reagent. As is known in the field, physically more compact circular polymers occupy smaller hydrodynamic volumes, thus, exhibit lower-MW readings on the SEC spectra than linear analogs.[68] We hypothesize that after short thermal depolymerization, the "hypothetically cyclic" Cp polymer would change to a linear conformation, leading to an SEC trace in the higher-MW region. However, due to the incorporation of Cp units across the polymer backbone, **Pol 1** also starts to depolymerize 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 depolymerization at 150 °C (Supporting Figures S98 and S101). Given this challenge, we also monitored the polymerization process and tracked the chain ends using ^{1}H 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 effects on the polymerization, but no improvement was observed (Supporting Figure S104). Of the inhibitors examined, BHT most efficiently prevented the degradation of Cp materials and resulted in the optimal MW. Polyaddition can also be haunted due to other reasons than decomposition, such as reaching a thermodynamic equilibrium, ceiling temperature,[69] or limitations caused by 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 effect the

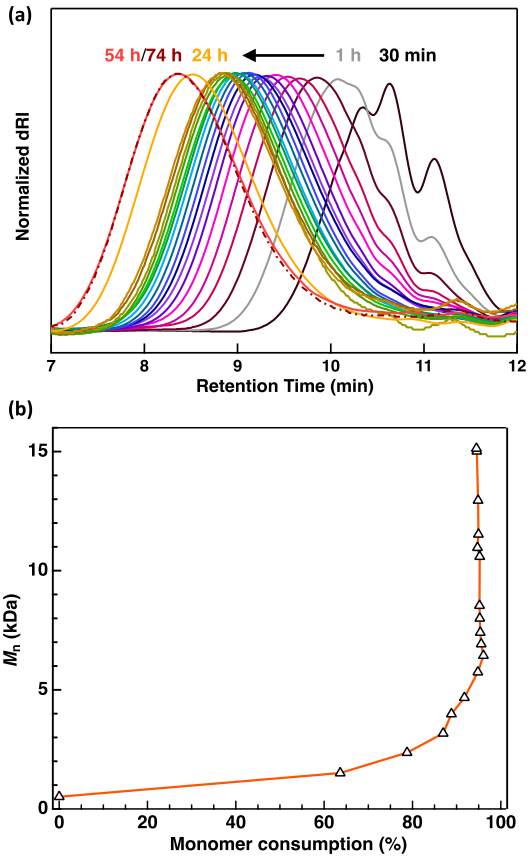

Figure 4. (a) The polymerization of **M1** (with 5 mol % BHT) at 90 °C was monitored throughout the course of 74 h with the SEC traces recorded at 30 min intervals between 0.5 and 8 h and then at 24, 54, and 74 h. The highest MW was obtained at 54 h. (b) The monomer consumption from ^{1}H NMR spectra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

DP[33,51] and influence the polymerizing behaviors. To determine whether 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 a higher MW despite the faster kinetics of Cp and maleimide, as reported in the literature.[39,45,46,72–75]

Thermo-Selective Recycling of Cp Homopolymers. To demonstrate the reversible DA design, selected homopolymers were subjected to recycling experiments by first depolymerization at 150 °C (the onset of rDA temperature range) and then repolymerization at 90 °C in the same pot without solvent and purification throughout the closed-loop process. All materials were characterized via standard chloroform SEC. Specifically, hydrogenated polybutadiene 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 depolymerization was monitored at 5, 15, and 30 min (Figure 5a). **Pol 4** reverted to smaller oligomers within 5 min. Heating the material for longer time (15 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 depolymerized material was determined to possess M_n of 23

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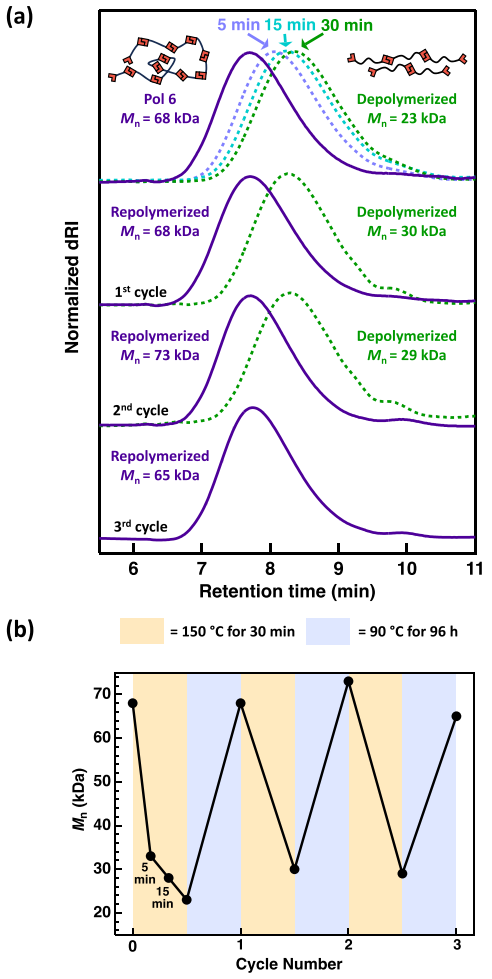

Figure 5. (a) Hydrogenated polybutadiene integrated with Cp dimers (**Pol 4**) was subjected to 3 cycles of de- and repolymerization processes with the addition of 1 wt % BHT in the absence of solvents. The first cycle involves the heating of **Pol 4** (M_n = 68 kDa) at 150 °C for 5, 15, and 30 min (top SEC traces). **Pol 4** was efficiently depolymerized (M_n = 68 to 23 kDa) after 30 min. No purification was performed as the resulting oligomer (M_n = 23 kDa) was directly subjected to repolymerization (i.e., 90 °C for 96 h). 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 repolymerization patterns. (b) The 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.

kDa (DP_n of ~4, contributing to ~70% depolymerization efficiency). Repolymerization was achieved by heating the lowest-MW oligomers (23 kDa, dotted-green SEC trace from the graph in Figure 5a) at 90 °C, for 96 h, following the original optimal polymerization conditions for **Pol 4**. The MW was fully recovered from 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,b).

The de- and repolymerization of **Pol 1**, **Pol 2**, **Pol 3**, and **Pol 6** were also performed under 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 depolymerized to oligomers with M_n of 5 kDa, which were subsequently repolymerized. The recovered material displays a higher-MW range compared to that of the original polymer (Supporting Information, Figure S114). **Pol 1** and **Pol 6** were successfully degraded upon heating but unexpectedly did not show efficient repolymerization behaviors, regardless of the varied de- and repolymerization conditions (e.g., change in the amount of BHT, purification of depolymerized mixtures, repolymerization with different solvents and temperatures; more details are described in Supporting Information, Section 1.16). Of note, these polymers contain higher concentrations of Cp and 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 repolymerization.[76] As aforementioned, critical purity of the oligomer chain ends is required to reform the parent polymers. Therefore, minimal degradation of Cp chain ends or ester linkages can have detrimental effects on repolymerization. When **Pol 6** was heated for a shorter amount of time (15 min rather than 30 min), the repolymerization was 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, thus, contains a 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 close to that of the original polymer (Figure S122). ^{1}H NMR spectra of the depolymerized materials were also collected for **Pol 1**−**4** and **Pol 6**, revealing the Cp chain ends (Supporting Figures S113, S115, S117, S121, and S123). In this work, only the recycling of a homopolymer was demonstrated; nevertheless, uprecycling with differently functionalized dienophiles is feasible and under ongoing investigation.

CONCLUSIONS

We demonstrate a new and straightforward methodology for preparing high-MW recyclable thermoplastics, utilizing single-component cyclopentadiene derivatives and the Diels−Alder polymerization/depolymerization. In this initial study, we synthesized and characterized six Cp homopolymers 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 depolymerization behaviors, except for the substances that contain high amounts of Cp and ester linkages. Here, unavoidable thermal degradation presumably contributed to the complications during the repolymerization process. Remarkably, the hydrogenated polybutadiene modified with Cp units (**Pol 4**) displays the ability to efficiently repolymerize and depolymerize 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, the synthesis and characterization of the recyclable Cp homopolymers present insights into their 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 the Cp-dimer that affect the material

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properties. We believe that this work can establish a mild and universal thermo-selective recycling strategy that will expand the design and construction of sustainable thermoplastics. Furthermore, in the realm of mixed plastics, polymers modified with Cp dimer units can be thermoselectively depolymerized in the presence of other traditional polymers. Assuming the reactive Cp chain ends after depolymerization, the repolymerization of a mixture of drastically different polymers to form new types of recycled materials can also be realized.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.4c05952.

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

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Author Contributions

T.M.T 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

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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, poly(dimethylsiloxane); NMR, nuclear magnetic resonance

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