Polyheptenamer: A Chemically Recyclable Polyolefin Enabled by The Low Strain of Seven-Membered Cycloheptene

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Keywords: depolymerization, polyheptenamer, cycloheptene, low ring strain

Abstract: Low-strain cyclic olefin monomers, including five-membered, six-membered, eight-membered, and macrocyclic rings, have been recently exploited for the synthesis of depolymerizable polyolefins via ring-opening metathesis polymerization (ROMP). Such polyolefins can undergo ring-closing metathesis depolymerization (RCMD) to regenerate their original monomers. Nevertheless, the depolymerization behavior of polyolefins prepared by ROMP of seven-membered cyclic olefins, an important class of low-strain rings, still remains unexplored. In this study, we demonstrate the chemical recycling of polyheptenamers to cycloheptene under standard RCMD conditions. Highly efficient depolymerization of polyheptenamer was enabled by Grubbs' second-generation catalyst in toluene. It was observed that the monomer yields increased when the depolymerization temperature increased and the starting polymer concentration was reduced. A near-quantitative monomer regeneration (> 96%) was achieved within one hour under dilute conditions (20 mM of olefins) at 60 °C. Moreover, polyheptenamer exhibited a decomposition temperature above 430 °C, highlighting its potential as a new class of thermally stable and chemically recyclable polymer materials.

1. INTRODUCTION

Synthetic polymers have become a ubiquitous part of our daily lives because of their light weight, durability, flexibility, and cost effectiveness. Nevertheless, the current recycling of end-of-life polymer wastes is rather limited, with the vast majority (> 90%) of them ending up in landfilling and incineration, which have resulted in serious environmental issues.[1,2] Moreover, the traditional mechanical recycling of polymer wastes typically produces secondary raw materials with lower quality compared to original polymer products.[3] To attenuate the negative environmental impact of the polymer wastes and improve the value of recycled products, it is highly desirable to develop closed-loop recycling systems that would produce no waste and regenerate the products with same quality.[4]

Depolymerization is a promising strategy to enable the closed-loop chemical recycling of polymer materials.[4-7] In a depolymerization process, polymers would be converted back into their constituent monomers, which can be repolymerized to form the new polymer products. In the past decade, efficient depolymerization has been achieved in a library of synthetic polymers prepared by various chain-growth polymerization techniques such as radical polymerization,[8-13] ionic ring-opening polymerization,[14-17] coordination ring-opening polymerization,[18,19] nucleophilic aromatic ring-opening polymerization,[20] and ring-opening metathesis polymerization (ROMP).[21-27] Among those depolymerizable polymers, polyolefins made by ROMP have attracted an increasing interest because of their thermally stable all-hydrocarbon backbones, and relatively mild depolymerization conditions (e.g., 20 – 60 °C and a low loading of metathesis catalyst).[6]

Low-strain cyclic olefin monomers are ideal building blocks for the ROMP synthesis of depolymerizable polyolefins. The resulting polyolefins are able to undergo ring-closing metathesis depolymerization (RCMD) to recover the original monomers because of their low ring strain energies (RSE).[6] To date, a series of low-strain cyclic olefins including 5-membered,[21,28-30] 6-membered,[26,27] 8-membered,[23-25] and macrocyclic rings,[31,32] have been used for producing chemically-recyclable polyolefins. While 7-membered lactone monomers have been utilized in synthesizing chemically recyclable polyesters,[33,34] to the best of our knowledge, depolymerizable polyolefins based on 7-membered cyclic olefin monomers have not yet been reported. Since the RSE of 7-membered cycloheptene is very similar to that of the 5-membered cyclopentene,[35,36] we hypothesized that the polyheptenamers produced by ROMP of cycloheptene would be depolymerizable under standard RCMD conditions. Herein, we systematically investigate the depolymerization behavior of polyheptenamers. Various reaction parameters such as the solvent, initial polymer concentration, and temperature were screened to optimize the depolymerization performance. It was found that a higher temperature and a lower olefin concentration led to a higher monomer yield. Notably, a near-quantitative recovery of cycloheptene (> 96%) was achieved within 60 min with 20 mM of olefins in toluene at 60 °C. Furthermore, polyheptenamer displayed a high decomposition temperature (> 430 °C), suggesting its promise as a chemically recyclable and thermally stable material.

2. RESULTS AND DISCUSSION

2.1. ROMP of Cycloheptene

The RSE of cyclic olefin monomers plays a critical role in the chemical recyclability of their corresponding polymers.[6] To enable both ROMP and RCMD pathways, a suitable RSE of monomers would range from 4 to 6 kcal/mol according to previous work.[25-27,30] In view of this, we began our study by calculating the RSEs of common cycloalkenes with various ring sizes from 5 to 8 (**Supporting Figures S1-S4**). The computed RSE values of those cycloalkenes are in good agreement with previous literature.[35-37] Among those monocyclic alkenes, only cyclopentene (RSE = 5.81 kcal/mol) has been demonstrated feasible in both its polymerization and the depolymerization of resulting polypentenamer (**Figure 1A**).[21,30] Cyclooctene possesses a relatively high RSE of 12.79 kcal/mol, which facilitates its polymerization but discourages the depolymerization of polyoctenamer.[23,35] On the other hand, the quite low RSE of cyclohexene (1.8 kcal/mol) renders its polymerization thermodynamically disfavored.[38] Cycloheptene has a very similar computed RSE (6.26 kcal/mol) in comparison to that of cyclopentene. Therefore, we reasoned that cycloheptene would be a suitable monomer for the ROMP synthesis of depolymerizable polyolefins (**Figure 1B**).

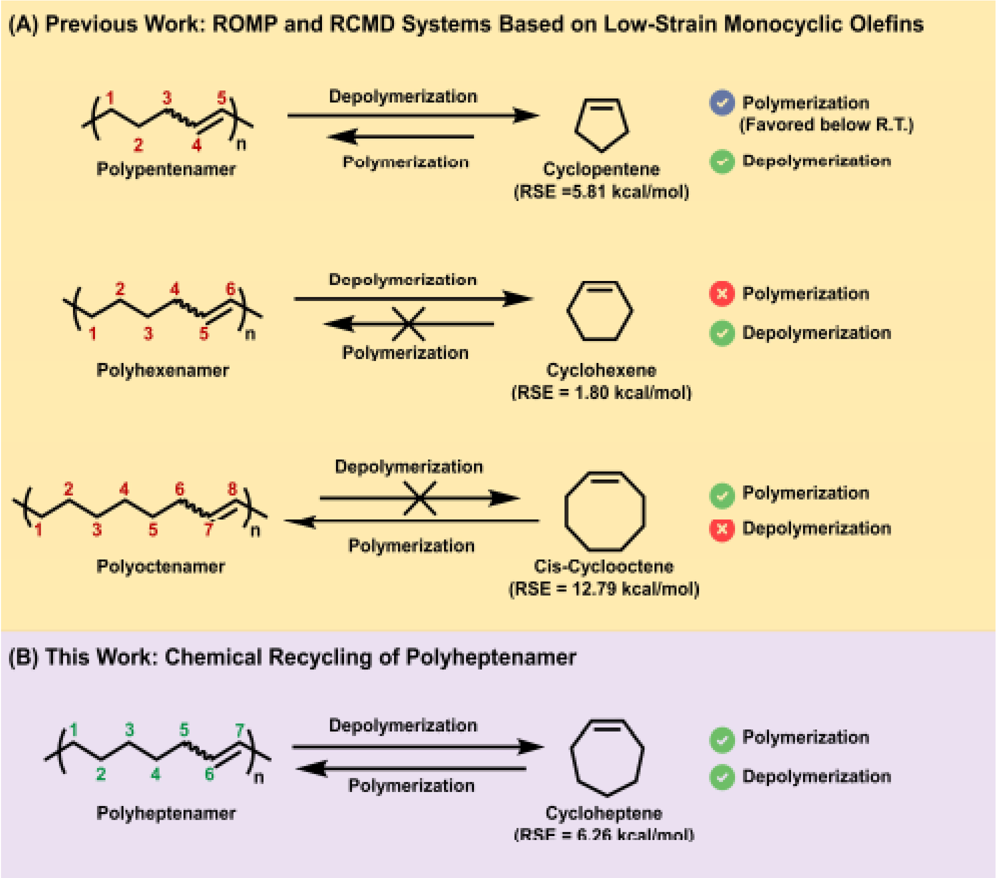

Figure 1. Chemical recyclability of polyalkenamers based on common low-strain cycloalkenes. (A) ROMP and RCMD performance of cyclopentene, cyclohexene, and cyclooctene. (B) Chemical recycling enabled by ROMP of cycloheptene and RCMD of polyheptenmaer. The ring strain energies of cycloalkenes were calculated by density functional theory (DFT) using Spartan software.

To discern the temperature effect on polymerization, we performed ROMP of cycloheptene in toluene at different temperatures using Grubbs' third-generation catalyst (G3). Unlike ROMP of cyclopentene which monomer conversion at equilibrium is highly temperature-dependent,[30,35] little variation in monomer conversion was observed at the investigated temperatures (0, 19, and 30 °C) for the ROMP of cycloheptene (**Figure 2 and Supporting Figure S5**). This phenomenon can be potentially attributed to a favorable entropic pennalty associated with the medium ring size of cycloheptene.[22] Compared to cyclopentene, the ring size of cycloheptene is larger and would gain more rotational and vibrational entropy upon being openned to the linear polymer state.[22,36,39] Additionally, the loss in translational entropy during the polymerization of cycloheptene is theoretically lower than that during the polymerization of cyclopentene.

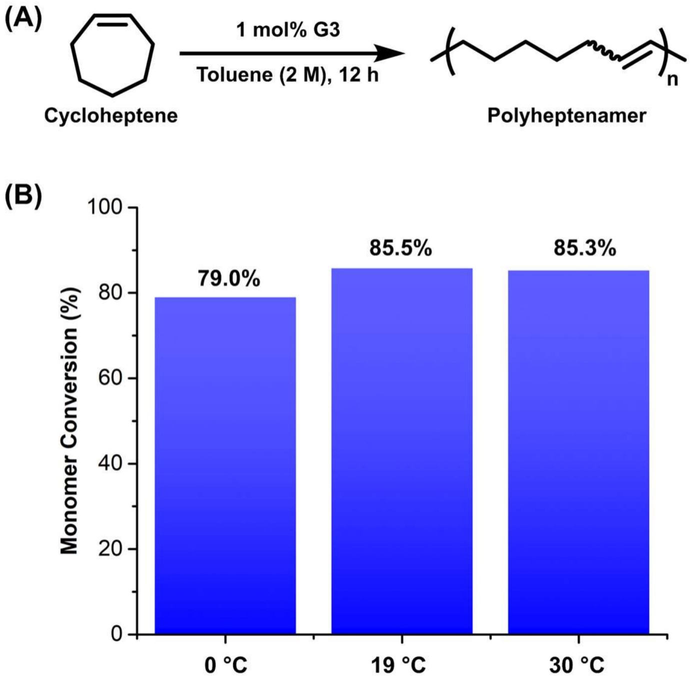

Figure 2. ROMP of cycloheptene at various temperatures. (A) G3-catalyzed ROMP of cycloheptene in toluene; (B) Monomer conversion as a function of polymerization temperature.

Next, a series of polyheptenamers (P1-P3) with different degrees of polymerization was achieved by varying the ratio of cycloheptene to G3 (**Table S1 and Figure 3**). ^{1}H and ^{13}C NMR spectroscopy verified the chemical structure of polyheptenamer, indicating that trans-alkene is predominant in the polymer backbone (**Figure 3A and Figure S6**). The number-average molecular weights of resulting polyheptenamers determined by size exclusion chromatography (SEC) are larger than those theoretical values (**Table S1**). This disparity can be ascribed to the different hydrodynamic volumes of polystyrene standards and polyheptenamers. The broad molecular weight distributions ($Đ$ = 1.5-1.8) observed can be attributed to chain transfer events resulting from the secondary metathesis of the unhindered polyheptenamer backbone.

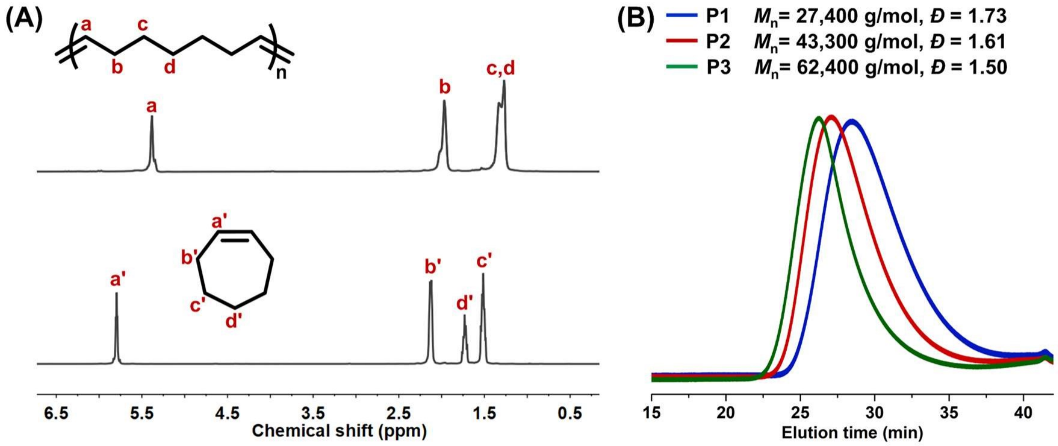

Figure 3. Characterization of polyheptenamers. (A) ^{1}H NMR spectra of polyheptenamer (P1) and cycloheptene; (B) SEC traces of polyheptenamers with different molecular weights.

2.2. Ring-Closing Metathesis Depolymerization of Polyheptenamer

To shed light on the depolymerizability of polyheptenamers, we systematically investigated the depolymerization behavior of P1 under various conditions (**Table 1**). The depolymerization of P1 was first attempted in $CDCl_3$ at 40 °C using Grubbs' second generation catalyst (G2). However, only low yields of cycloheptene (< 21%) were formed even at 20 mM of olefins (**Entries 1 and 2 in Table 1, and Supporting Figures S7 and S8**). To facilitate the depolymerization study at a wide range of temperatures, we further switched the solvent to toluene because of its high boiling point.

Table 1. Depolymerization performance of polyheptenamer under different conditions

Entry[a]	Olefin Concentration (mM)	Temperature (°C)	Solvent	Time (h)	Recovered Monomer (%)[b]
1	200	40	$CDCl_3$	12	11.6
2	20	40	$CDCl_3$	12	20.1
3	200	60	Toluene-d_8	12	58.5
4	100	20	Toluene-d_8	12	44.0
5	100	40	Toluene-d_8	12	55.9
6	100	60	Toluene-d_8	12	66.2
7	50	60	Toluene-d_8	12	78.7
8	20	60	Toluene-d_8	1	96.0

a)Depolymerization experiments were catalyzed by 2.0 mol% G2 under argon atmosphere; b)Monomer regeneration yields were estimated by ^{1}H NMR spectroscopy.

The role of temperature in depolymerization performance was elucidated at 100 mM of olefins (**Entries 4-6 in Table 1, and Figure 4A and 4B**). Based on ^{1}H NMR analysis, the olefinic proton signals of both cycloheptene (5.79 ppm) and its cyclic dimer: *trans, trans*-cyclotetradeca-1,8-diene[40] (5.15 ppm) were observed after the depolymerization (**Figure 4B**). The monomer/dimer ratio was 53: 47 when the depolymerization was performed at 20 °C. As the depolymerization temperature increased to 60 °C, the selectivity of monomer product over the dimer was significantly improved, as evidenced by a high monomer/dimer ratio (86:14). Consequently, the monomer yield increased from 44.0% at 20 °C, to 66.2% at 60 °C.

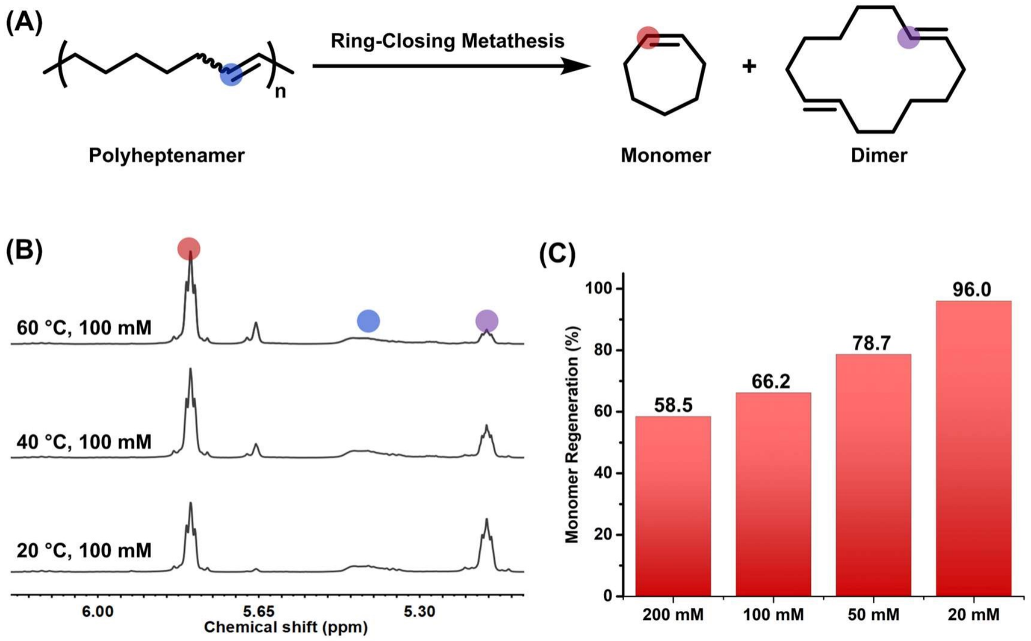

Figure 4. Depolymerization study of polyheptenamer under different conditions. (A) Schematic illustration of depolymerization of polyheptenamer; (B) ^{1}H NMR spectra of depolymerization products generated at different temperatures; (C) Monomer regeneration yield as a function of olefin concentration. The depolymerization was carried out at 60 °C for 12 h.

We further examined the concentration effect on the depolymerization efficiency at 60 °C (**Entries 3, 6, 7, and 8 in Table 1, and Figure 4C**). As shown in **Figure 4C and supporting Figure S9**, the monomer yields gradually increased as the concentration of polymer decreased. More than 78% of monomer was recovered when the olefin concentration was below 50 mM. Remarkably, a near-quantitative monomer regeneration (> 96 %) was observed within 60 min at 20 mM of olefins (**Figure 5A and 5B**). SEC analysis further corroborates the NMR result by showing the complete disappearance of polymer signal, and the appearance of monomer peak after the depolymerization (**Figure 5C**).

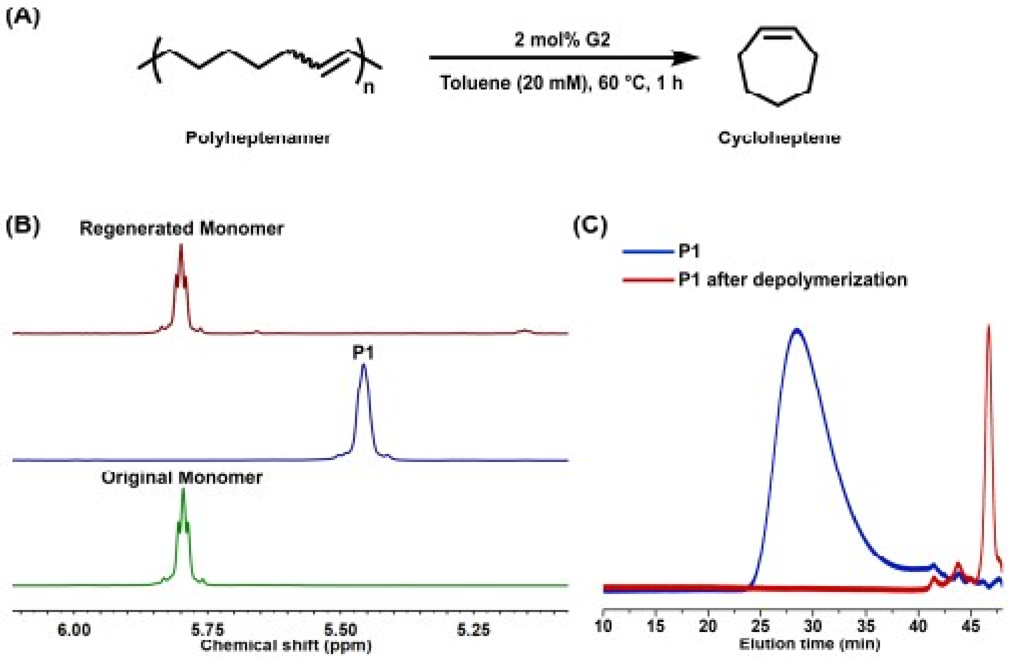

Figure 5. Quantitative depolymerization of polyheptenamer under optimized conditions. (A) RCMD of polyheptenamer enables the exclusive and fast production of cycloheptene with 20 mM of olefins in toluene at 60 °C; (B) Partial ^{1}H NMR spectra of original cycloheptene, P1, and the regenerated cycloheptene in toluene-d_8; (C) SEC traces of P1 and the depolymerization product. The depolymerization was carried out in toluene with 20 mM of olefins at 60 °C for 1 h.

To further elucidate the mechanism of depolymerization, we conducted a kinetic study on the depolymerization of polyheptenamer at 20 °C under dilute conditions (20 mM of olefin) (**Figures S10 and S11**). As the depolymerization proceeded, we observed a steadily increase in the monomer concentration, indicating the progressive depolymerization of the polymer. Interestingly, the dimer concentration gradually increased over the first hour, suggesting a pathway from polymer to dimer during the initial stage of depolymerization. However, upon the full consumption of the polymer, a decrease in dimer concentration was observed, indicating its further transformation into monomer species (**Figure S11**). The depolymerization reached equilibrium after 12 h, resulting in the formation of 78% monomers and 22% dimers.

In principle, depolymerization is an entropy-driven process ($\Delta S > 0$), favored at lower concentrations and higher temperatures. At lower concentrations, the formation of monomers leads to a greater increase in translational entropy compared to dimers. Furthermore, higher temperatures promote the entropically favored transformation of dimers into monomers, resulting in a higher monomer recovery.

2.3. Thermal Properties of Polyheptenamer

Finally, the thermal properties of polyheptenamer were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (**Figure 6**). According to TGA thermogram, P1 displayed a high decomposition temperature at 5% weight loss ($T_{d,5\%}$ = 432.3 °C), which is consistent with the excellent thermal stability of all-hydrocarbon polymer backbone (**Figure 6A**). DSC further revealed a melting temperature (T_m = 48.8 °C) and a crystallization temperature (T_c = 19.9 °C) of P1, suggesting a semicrystalline structure of polyheptenamer (**Figure 6B**). This result can be attributed to a high degree of trans-configuration in the as-synthesized polyheptenamer that facilitates the crystallization of linear polymer chains.[41]

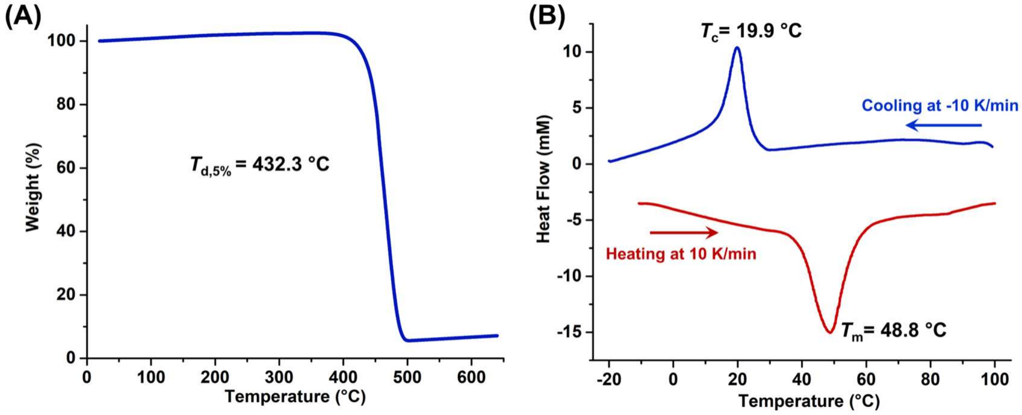

Figure 6. Thermal properties of polyheptenamer. (A) TGA thermogram of P1; (B) DSC thermogram of P1. T_m and T_c were obtained from the second heating scan and the second cooling scan, respectively.

3. Conclusion

In summary, we have unveiled the depolymerization behavior of polyheptenamers prepared by ROMP of cycloheptene. The low RSE of cycloheptene enables the efficient depolymerization of polyheptenamers under typical RCMD conditions. Notably, polyheptenamer can fully revert to cycloheptene monomers under dilute conditions (20 mM of olefins) at 60 °C in the presence of G2, demonstrating its chemical recyclability. Moreover, the all-hydrocarbon backbone renders polyheptenamers highly thermally stable up to 430 °C. We envision that this study will pave the way for a new class of chemically recyclable polymer materials based on seven-membered cyclic olefin monomers. The development of functional polyheptenamers with tunable thermomechanical properties are currently underway in our lab.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This study is based upon work supported by a LEAPS-MPS award from the National Science Foundation under grant no.[CHE-2316842], and the donors of ACS Petroleum Research Fund under Undergraduate New Investigator Grant [66137-UNI7]. H. S. served as the Principal Investigator on ACS PRF [66137-UNI7] that provided support for A. R.

Received: ((will be filled in by the editorial staff))
Revised: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

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