Dynamic Remodeling of Covalent Networks via Ring-Opening Metathesis Polymerization

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S *Supporting Information*

ABSTRACT: Reversible transformations in bulk polymers offer numerous possibilities for materials remodeling and reprocessing. While reversible systems based on dynamic covalent chemistry such as the Diels−Alder reaction and transesterification have been intensively studied to enable local bond dissociation and formation, reports regarding the reversion from bulk network polymers to monomers are rare. Herein, we report a reversibly polymerizable system based on ring-opening metathesis polymerization of cyclopentene derivatives in the bulk state. The network polymer is thermodynamically stable and mechanically robust at room temperature and readily depolymerizes at elevated temperatures to yield liquid monomers that are repolymerized to cross-linked polymers by simply cooling to room temperature. This reversible process was characterized by differential scanning calorimetry and rheological tests.
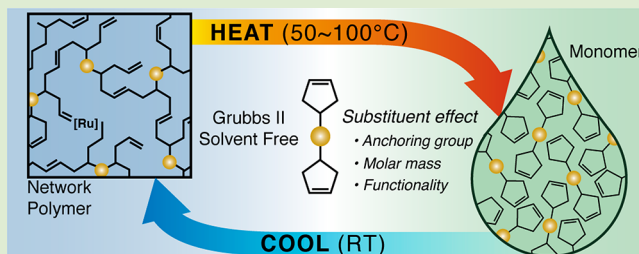
Remodeling is an important process in biological systems for resiliency and maintenance.[1,2] A common example is the remodeling of actin filament, a supramolecular polymer, that allows for the dynamic alterations of cellular organization.[3] Upon certain chemical stimuli, actin filaments are depolymerized; the resulting monomers are repolymerized to reshape the cell to a new environment. Inspired by the biopolymers, synthetic polymers capable of remodeling may have the potential to reconfigure and adapt themselves to a changing environment by removing and replacing the activated regions with newly synthesized materials.

A promising materials candidate for remodeling is covalent-adaptable networks (CANs) where reversible chemical bonds are incorporated.[4−8] As heat is one of the simplest stimuli, thermoresponsive CANs have been widely studied for shape memory and self-healing applications. Many chemistries have been utilized, including reversible addition (or condensation), such as the Diels−Alder reaction, and reversible exchange reactions, such as transesterification and transimination. These CANs are reconfigurable and recyclable while still possessing the mechanical benefits of traditional thermosets. At elevated temperatures, CANs partially depolymerize, resulting in linear polymers or less-cross-linked systems with decreased moduli. Subsequent cooling allows repolymerization that affords networks with higher moduli. While these systems are reversible, depolymerization often leads to irreversible degradation of the polymer networks, since the ceiling temperature (T_c) is typically high.[9] Here, we report a reversibly polymerizable system based on ring-opening metathesis polymerization (ROMP) of cyclopentene derivatives with the interconversion between network polymers and neat liquid

monomers. As shown in Scheme 1, network polymers are readily depolymerized upon heating to liquid monomers,

Scheme 1. Schematic of the Depolymerization−Repolymerization Cycle of Network Polymers Based on ROMP
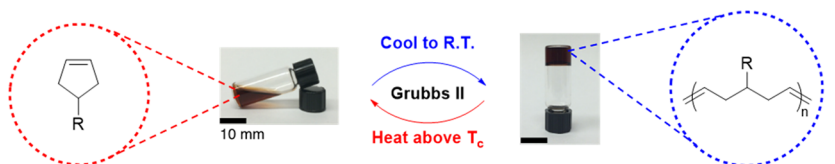

Network polymer   Monomer
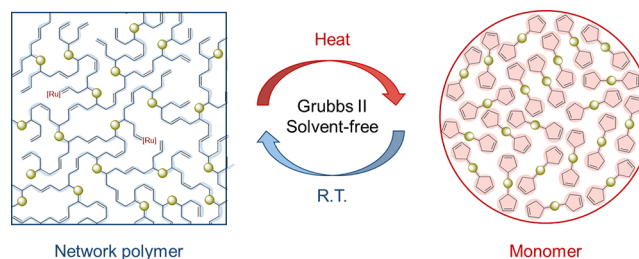
which are transported and reshaped; the subsequent repolymerization affords network polymers by simply cooling the system to room temperature.

We envisioned ROMP as a promising system for remodeling for two main reasons. First, dynamic covalent bond formation has been demonstrated in olefin metathesis both in solution and in the bulk state.[10−12] Second, polymerizability in ROMP is governed by ring strain, which is tunable by varying the ring structure of the monomers.[13,14] The ideal monomer for remodeling purposes will efficiently polymerize at room

**Table 1. Reversible Polymerization of Substituted Cyclopentene Monomers**

Entry	1a	1b	1c	1d	1e	1f	1g	1h	1i
Monomer									
T_c(solution)^a (°C)	35 ± 2	49 ± 1	31 ± 1	-14 ± 2	-35 ± 3	-25 ± 1	-15 ± 1	-25 ± 1	-15 ± 2
Extrapolated T_c(neat)^b (°C)	185 ± 3	386 ± 3	92 ± 5	67 ± 5	70 ± 3	59 ± 4	45 ± 3	48 ± 1	55 ± 2
$T_d{}^c$ (°C)	not obsd^d	not obsd^d	82 ± 4	62 ± 1	82 ± 2	60 ± 3	51 ± 2	68 ± 2	52 ± 2
Monomer conversion^e (%)	92 ± 2	84 ± 1	78 ± 4	84 ± 3	69 ± 2	63 ± 2	55 ± 3	68 ± 5	24 ± 2

^{a}Calculated as T_c(solution) = $\Delta H/\Delta S$, where ΔH and ΔS were obtained from VT-NMR. The polymerization was performed in THF-d_8 with 0.22 mol % catalyst loading. ^{b}Calculated as T_c(neat) = $\Delta H/(\Delta S + R \ln[M]_{max})$, where $[M]_{max} = \rho$ (g/L)/M (g/mol). ^{c}Determined by DSC with a ramping rate of 10 °C/min. ^{d}Degradation of the polymer backbone occurred before depolymerization. ^{e}Determined by ^{1}H NMR after equilibrium.

temperature to afford mechanically robust polymers which will fully depolymerize upon a mild temperature stimulus. Previous studies suggest that cyclopentene is a promising candidate since the conversion from monomer to polypentenamer is dramatically affected by the applied temperature.[15,16] However, the polypentenamers synthesized from cyclopentene or 3-cyclopenten-1-ol can only be depolymerized in solution since the ring strain energy (RSE) of these two monomers are too large to favor depolymerization in the bulk. Thus, we hypothesized that incorporating bulky substituents into the cyclopentene ring will reduce the ring strain and tune the depolymerizability to a desirable range.

To test this hypothesis, we first quantitatively evaluated the polymerizability of substituted cyclopentenes by T_c both in solution and neat conditions (see Supporting Information for details).[13,14] T_c in solution was determined by variable-temperature nuclear magnetic resonance (VT-NMR). The catalyst loading and the type of the catalyst have negligible effects on thermodynamics of the polymerization.[15] Grubbs' second generation catalyst (Grubbs II) was chosen due to its excellent solubility in neat cyclopentene monomers. By plotting $\ln([M]_e)$ against $1/T$, enthalpy change (ΔH) and entropy change (ΔS) were determined based on the slope and y-intercept, and T_c was calculated as T_c(solution) = $\Delta H/\Delta S$ (Figures S1 and S2 and Tables S1−S9). This T_c(solution) is extrapolated to bulk polymerization according to T_c(neat) = $\Delta H/(\Delta S + R \ln[M]_{max})$, where $[M]_{max}$ depends on the density and molar mass of the monomer.[17] Compared to 1a and 1b, monomers with bulkier substituents (1c−1i) possess much lower T_c values, as summarized in Table 1. These results indicate that depolymerization of the substituted polypentenamers in the neat state is feasible upon a mild temperature stimulus. We further characterized this behavior by differential

scanning calorimetry (DSC) to measure the depolymerization temperature (T_d) of the equilibrated monomer-polymer mixture from bulk polymerization at room temperature (Figure S4). Except for 1e and 1h that form hydrogen-bonding which leads to higher T_d than extrapolated T_c(neat), T_d agreed well with T_c(neat) (Figure S5). This not only confirms the reliability of extrapolation from VT-NMR but also implies DSC as a straightforward empirical method to estimate the T_c(neat) of low-strain monomers.

While ring size is often considered as the main contributor to ring strain, substituents also have a large influence on the thermodynamics of ROMP. Functional groups that directly attach to the cyclopentene ring are a key determinant of ring strain and polymerizability. DFT calculations show that 1b has a slightly higher RSE of −6.77 kcal/mol than 1a (−5.44 kcal/mol), and 1h possesses an even lower RSE (−4.9 kcal/mol).[16] These calculated results show good agreement with our experimental observations. In general, polymerizability decreases in the order of −OR > −COOR > −CH$_2$OR. For example, polymers resulting from 1d depolymerize at a higher temperature than those from 1g and 1i. While 1g and 1i possess similar T_d around 50 °C, 1i has a much lower monomer conversion. Monomer 1j with −CH$_2$OTBS substituent showed no evidence of polymerization under neat conditions at R.T., which further confirms the lower polymerizability of monomers with −CH$_2$OR (Figure S3). Molecular weight also contributes to the polymerizability. While T_c(solution) value reflects the ring strain in a monomer, T_c(neat) value is a combination of ring strain, molecular weight, and density of the monomer. Monomers with lower densities or larger molecular weights tend to have lower T_c(neat) values than those with similar ring strain. For example, as the substituent size increases from R = COOH to
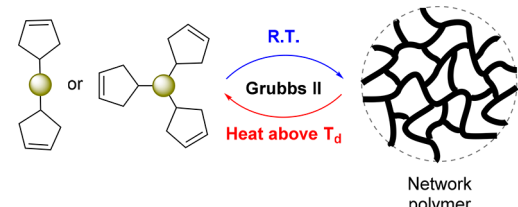
R = COOBn, T_c(neat) and monomer conversion of **1e**, **1f**, and **1g** decrease accordingly. This phenomenon is likely due to the fact that larger substituents result in decreased ΔS, which decreases the propensity of polymerization.
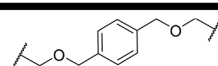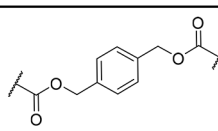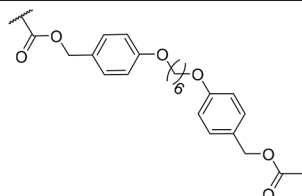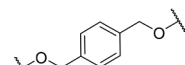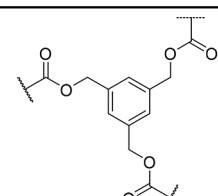
While monofunctional cyclopentene derivatives only form linear polymers with poor mechanical properties (Figure S9), polymerization of multifunctional monomers affords CANs that depolymerize at elevated temperatures, which meets the criteria for remodeling. We then selected a series of multifunctional monomers (**2a**−**2d** and **3a**) with different anchoring groups to investigate their polymerizability. Because **2a** and **2d** are solids at room temperature with melting points of 44 and 41 °C, bulk polymerization was first initiated at 50 °C for 30 min before being brought back to room temperature for 24 h. As shown in Table 2 and Figure S6, T_d and monomer conversion follow the same trend as the monofunctional monomers: **2d** > **2b** > **2a**. To further verify the effect of the anchoring group, **2c** (melting point 75 °C), which has the same ester anchor group as **2b**, but possesses much larger molecular weight, was also examined. It was found that the molecular weight has a negligible effect on polymerization and depolymerization behavior. In terms of T_d and monomer conversion under the same bulk polymerization conditions, **2b** and **2c** were nearly identical, indicating that the anchoring group effect is a main contributor to the polymerizability of cyclopentene derivatives. For trifunctional monomer **3a**, depolymerization occurred at a higher temperature than **2b** due to a higher degree of cross-linking density but its conversion to network polymer was the same as **2b** under the same polymerization conditions. In general, as the functionality of cyclopentene increases (from monofunctional to trifunctional monomer), polymerizability increases accordingly.

Besides varying T_d by different substituents, another approach to tune depolymerization is by copolymerization of two monomers with disparate values of T_d. To demonstrate this approach, we copolymerized **2b** and **1g**. Due to the similarity of these two comonomers in structure, they formed a uniform random copolymerized CAN and its depolymerization behavior was observed as a narrow endothermic peak on DSC (Figure S7). By introducing different amounts of comonomer **2b**, T_d of the CAN was varied between T_d(**1g**) and T_d(**2b**) linearly, as shown in Figure 1. The depolymerization behavior was further characterized by rheological measurements (Figures S10−S13 and Table S11). Elevating the temperature near T_d significantly depolymerized the solid network and resulted in a liquid as both viscoelastic storage modulus G' and loss modulus G'' dropped below the minimum torque resolution of the experimental setup.

With the establishment of tunable T_d, reversibility of the depolymerization−repolymerization process of the monofunctional system was evaluated. Equilibrium monomer conversion and number-average molecular weight (M_n) of the monomer−polymer mixture were monitored in the heating−cooling cycle (Figure 2, Figure S8, and Table S10). After initiation at 50 °C and subsequent polymerization at 25 °C of **1g** for 2 h, the monomer conversion and M_n increased to 51% and 41 kDa, respectively. Upon heating to 50 °C, depolymerization was favored, resulting in reduced monomer conversion and M_n to 13% and 2.1 kDa, respectively. The system exhibited a highly temperature-sensitive behavior, and this depolymerization−repolymerization was reversible for several cycles. The slight decrease in reversibility is likely a result of side reactions[18] and

Table 2. Reversible Polymerization of Difunctional and Trifunctional Monomers

Entry	Spacer ⬤	$T_d{}^a$ (°C)	Conversion^b (%)
2a		60 ± 1	79 ± 1
2b		76 ± 2	86 ± 2
		83 ± 3^c	78 ± 3^c
2c		76 ± 2^c	74 ± 1^c
2d		97 ± 2	92 ± 2
3a		89 ± 1	86 ± 1

^{a}Determined by DSC with a ramping rate of 10 °C/min. ^{b}Calculated from the unreacted monomers after 24 h polymerization at R.T. by ^{1}H NMR using mesitylene as the internal standard. ^{c}Polymerization was initiated at 80 °C for 30 min and then carried out at room temperature for 24 h.

shortened catalyst lifetime[19] at elevated temperatures, which leads to less active Ru carbene species.

Rheological measurements were then performed to investigate the reversibility of CAN from difunctional monomer **2b** by cycling the temperature between 70 and 25 °C. As shown in Figure 3 (top), 2 h polymerization at 25 °C afforded CANs with a $G'[1]$ = 1.78 MPa, where [1] refers to the first polymerization cycle. This modulus is within the typical range for a rubber elastic network. When heated to 70 °C, G' fell precipitously, indicating fast depolymerization; upon cooling to 40 °C, the liquid repolymerized almost immediately and after developing at 25 °C for the same 2 h, G' recovered to a value of $G'[2]$ = 0.39 MPa (22% of $G'[1]$). After a second cycle of
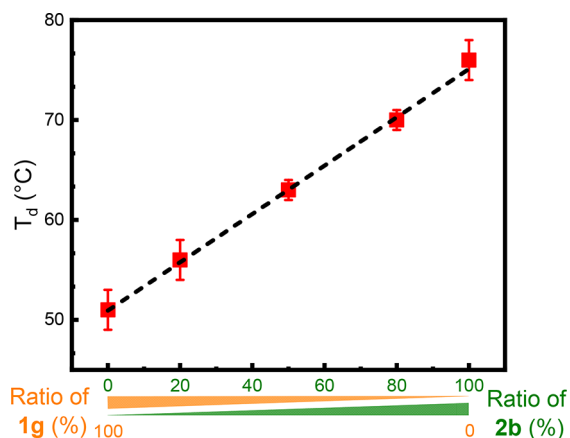
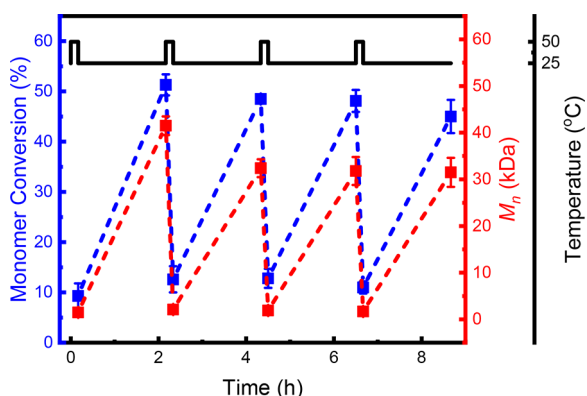**Figure 1.** Depolymerization temperatures of copolymers from different **1g:2b** ratios. $R^2 = 0.99$.

Figure 2. Multiple depolymerization–repolymerization cycles of **1g**. Monomer and catalyst (0.22 mol %) were mixed and cycled between 50 and 25 °C.

Figure 3. Rheological characterization at 1 rad/s of CANs from **2b** (top) and 1:4 copolymerization of **2b** and **1g** (bottom). Both samples were first initiated at 55 °C and cycled between 25 °C and T_d.

heating and cooling, G' was further reduced to 10% of G'[2]. One reason for the substantial loss of reversibility is that network polymers are much less mobile compared to the monofunctional system, which slows down the kinetics of metathesis. Another reason is the presence of irreversible side reactions at high temperatures, which is similar to the monofunctional system. This is also supported by reversibility experiments of the copolymerization system with a lower T_d. As demonstrated in Figure 3 (bottom), by copolymerizing **2b** and **1g** at a molar ratio of 1:4 with T_d of 55 °C, recovery efficiency was greatly improved to 54% and 60% within the same 2 h after the first and second cooling cycles, respectively. With this ROMP system, we have shown polymerizable materials capable of reversibly transitioning between a stiff solid (G' in MPa region), and a liquid (viscosity $\eta \approx 10^{-2}$ Pa·s, Figure S14) with moderate recovery efficiency on repolymerization.

We developed a series of CANs for remodeling applications based on ROMP. We demonstrated that varying the substituents on the cyclopentene ring affords tunable ceiling temperatures or depolymerization temperatures ranging from 50 to 100 °C. These neat cyclopentene monomers are polymerizable at room temperature, and the resulting polymers are readily depolymerized at elevated temperatures. This depolymerization-repolymerization process is triggered solely by temperature changes and is reversible for several cycles. For reversibility tests, we were able to improve the recovery
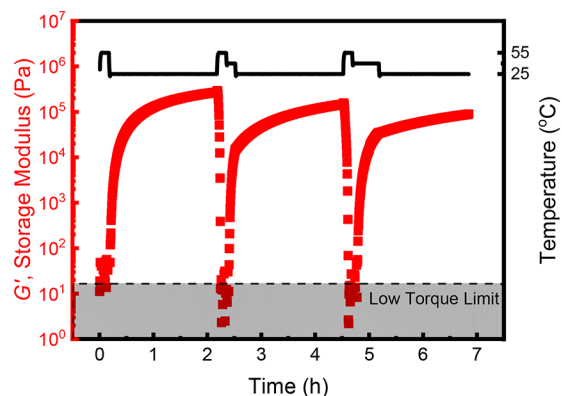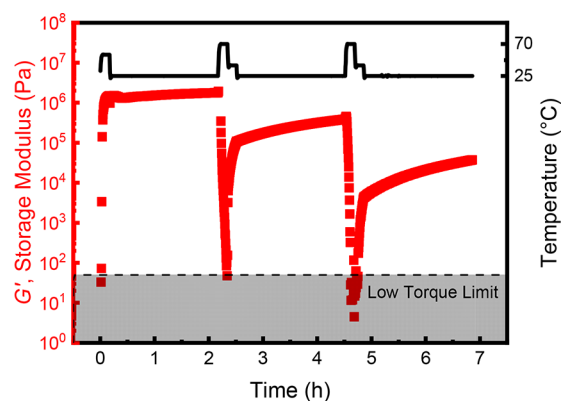
performance by lowering the depolymerization temperature via copolymerization. These results indicate the first step toward the engineering of reversibly polymerizable materials as only a mild temperature stimulus is needed to depolymerize the polymers into liquid monomers, which are transported and repolymerized to remodel the material system at room temperature.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacro-lett.8b00422.

> General experimental details, synthesis of cyclopentene derivatives, ceiling temperature measurement, DSC, and rheological characterization (PDF).

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Notes

The authors declare no competing financial interest.

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