Chemical Recycling of Polyolefins via Ring-Closing Metathesis

Depolymerization

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Abstract

The current insufficient recycling of commodity polymer wastes has resulted in pressing

environmental and human health issues in our modern society. In the quest for next-generation

polymer materials, chemists have recently shifted their attentions to the design of chemically

recyclable polymers that can undergo depolymerization to regenerate monomers under mild

conditions. During the past decade, ring-closing metathesis reaction has been demonstrated a

robust approach for the depolymerization of polyolefins, producing low-strain cyclic alkene

products which can be repolymerized back to new batches of polymers. In this review, we aim to

highlight the recent advances in chemical recycling of polyolefins enabled by ring-closing

metathesis depolymerization (RCMD). A library of depolymerizable polyolefins will be covered

based on the ring size of their monomers or depolymerization products, including five-membered,

six-membered, eight-membered, and macrocyclic rings. Moreover, current limitations, potential

applications, and future opportunities of RCMD approach will be discussed. It is clear from recent

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research in this field that RCMD represents a powerful strategy towards closed-loop chemical recycling of novel polyolefin materials.

1. Introduction

Since Hermann Staudinger proposed his famous macromolecular hypothesis in 1920, the field of polymer science has blossomed.^{1, 2} Numerous synthetic polymers with tunable thermal, mechanical, optical, and chemical properties have been developed and commercialized over the past century.³ Indeed, synthetic polymers are now ubiquitous in every aspect of our daily life, approaching a staggering production level of more than 367 million tons worldwide as of 2020.⁴ Nevertheless, less than 10% of synthetic polymer materials at the end of their usage life has been recycled, with the vast majority of polymer wastes ending up in landfills and incineration that have negative impacts on environment and human health.⁵⁻⁷ Moreover, the value of recycled polymer materials is compromised upon traditional mechanical recycling process which usually reduces the physicochemical properties of polymers.⁸

Depolymerization represents a promising solution for chemical recycling of polymer wastes. In principle, depolymerization of polymer wastes back into original monomers, and subsequent repolymerization would produce recycled polymer materials with the same physicochemical properties compared to original ones. $^{9-16}$ However, the current commercial polymers possess inherently high ceiling temperatures (T_c), above which the depolymerization would occur. For instance, thermal depolymerization or pyrolysis of polystyrene (T_c = 396 °C) is typically performed at temperatures of 400-900 °C, which require high cost in energy. Furthermore, thermal depolymerization of commercial polymers at elevated temperatures can lead to alternative degradation pathways and the generation of char. To facilitate the depolymerization process under mild conditions, it is highly desired to design depolymerizable polymers with low ceiling temperatures. Critically, such depolymerizable polymers would exhibit excellent thermal stability

in a kinetically trapped state, and depolymerization should be triggered only in the presence of a catalyst. 19

Ring-opening metathesis polymerization (ROMP) has been widely exploited in the synthesis of polyolefins that contain repeating alkene double bonds in the polymer backbone. 20-25 The development of well-defined metathesis catalysts has imbued state-of-the-art ROMP technique with excellent functional group compatibility and high resistance towards air and moisture, giving rise to various functional polymer materials.26-33 In a typical ROMP process, cyclic olefin monomers with high ring strain energy (RSE) can be polymerized into well-defined polyolefins with predetermined molecular weights and low dispersity. The release of ring strain energy (i.e., ΔH_o) upon the ring-opening event serves as the driving force and compensates the entropic loss $(\Delta S_p < 0)$ during the polymerization. The ceiling temperatures of polymers can be determined by Gibbs free energy equation: $\Delta G_p = \Delta H_p - T\Delta S_p$ when $\Delta G_p = 0.29, 34, 35$ Since the polymerization of high RSE monomers is more exothermic (ΔH_p is less negative) than that of low RSE monomers, the ceiling temperatures at which ΔG_p is 0 would be higher for polymers made via ROMP of high RSE monomers such as norbornene (RSE = 27.2 kcal/mol, T_c = 1000 K in bulk), ^{36, 37} rendering the resulting polyolefins non-depolymerizable under mild conditions. On the other hand, depolymerizable polyolefins with low ceiling temperatures are accessible by equilibrium ROMP of low RSE monomers such as cyclopentene (RSE = 5.3 kcal/mol, $T_c = 330 \text{ K}$ in 2.17 M monomer solution) and 2,3-dihydrofuran (RSE = 5.0 kcal/mol, T_c = 350 K in bulk).^{34, 38} Depolymerization of such low T_c polyolefins can be enabled via ring-closing metathesis (RCM) reaction in the presence of metathesis catalysts by adjusting conditions to shift the equilibrium to monomer formation (Figure 1).²⁹

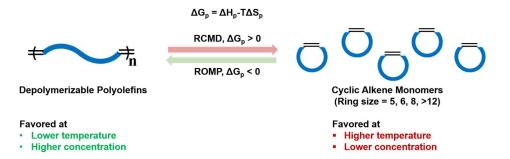


Figure 1. Closed-loop chemical recycling of depolymerizable polyolefins via ring-closing metathesis depolymerization (RCMD) and ring-opening metathesis polymerization (ROMP) of low-strain cyclic olefin monomers.

This review focuses on recent work on chemical recycling of polyolefins enabled by ring-closing metathesis depolymerization (RCMD). We will highlight the synthesis and depolymerization of various depolymerizable polyolefins according to the ring size of their monomers or RCMD products, covering five-membered, six-membered, eight-membered, and macrocyclic molecules (**Figure 2 and Table 1**). Furthermore, we will systematically evaluate the current challenges and future opportunities of RCMD approach for achieving a circular economy of polymers in the future.

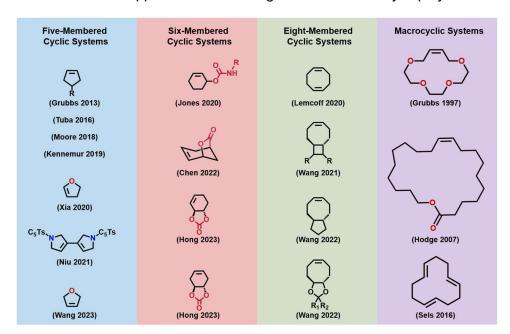


Figure 2. Representative cyclic depolymerization products or cyclic olefin monomers suitable for the synthesis of depolymerizable polyolefins.

 Table 1. Summary of representative depolymerizable polyolefins that can undergo RCMD.

Monomer Structure	ΔH _p (kcal/mol)	ΔS _p (cal/mol/K)	Depolymerization Conditions and Efficiency	Thermomechanical Properties	Ref.
<u></u>	-5.6	-18.5	HG2, R.T., 4 min	N/A	Tuba ³⁸
•			100%		
\bigcirc	-4.84	-18.7	G2, 50 °C, 10 min	Storage modulus: 1.78 MPa ^a	Moore ⁴²
OOBn			38%		
ç <mark>0</mark> >	-5.0	-19.4	G2, 60 °C, 150 min	$T_{\rm g}$ = -50.5 °C; $T_{\rm d}$ = 320 °C	Xia ³⁴
			>90%		
, o	-4.74	-13.9	G2, 40 °C, 24 h	T _g = 111-113 °C; T _d = 361 °C	Chen ⁴⁶
			93%	Storage modulus: 1.65 GPa	
				Young's modulus:3.8 ± 0.6 GPa	
				Tensile strength: 40.0 ± 10.9 MPa	
				Elongation at break: 76 ± 9%	
$\langle \overline{} \rangle$	-6.00	N/A	G2, 25 °C, 24 h	$T_{\rm g}$ = 62 °C; $T_{\rm d}$ = 316 °C	Hong ⁴⁵
00	(DFT)		>96%	Tensile strength: 27.7MPab	
0				Elongation at break: 95% ^b	
<u></u>	-2.8	-4.9	G2, 50 °C, 2 h	T _g = 100 °C	Wang ¹⁹
\mathcal{A}'			80-96%	Young's modulus: 1.40 ± 0.06 GPa	
o N Co				Tensile strength: 39 ± 5 MPa	
Ph				Elongation at break: 3.4 ± 0.3%	
	-1.7	-3.6	G2, 50 °C, 2 h	<i>T</i> _g = 18 °C	Wang ¹⁹
			94-98%		
	-2.9	-3.2	G2, 50 °C, 2 h	T _g = -33 °C; T _d = 405 °C	Wang ⁴⁹
\bigcirc			84%		

^aThe storage modulus was recorded for polymer network made by difunctional crosslinker. ^bThe tensile strength and elongation of break were recorded for the hydrogenated hydroxy-functional polymer.

2. Depolymerizable Polyolefins Based on Five-Membered Cyclic Monomers

Five-membered cyclopentene derivatives have attracted the most interest in producing depolymerizable polyolefins (i.e., polypentenamers) because of their adequate RSEs that allows for both ring-opening metathesis polymerization and ring-closing metathesis depolymerization under different conditions.^{29, 39, 40} Moreover, polypentenamers exhibit exceptional physical and mechanical properties, rendering them highly desired elastomer materials for industrial applications such as packaging and tire additives.^{40, 41}

In 2013, Tuba and Grubbs demonstrated the first example of ruthenium-catalyzed equilibrium ROMP of cyclopentene.³⁸ According to their thermodynamic investigation on the polymerization, the equilibrium concentrations of cyclopentene monomer was only dependent on the reaction temperatures, regardless of the catalyst type and loading. As the temperature increased from 0 to 30 °C, the equilibrium shifted towards depolymerized products, as evidenced by a gradual increase in monomer concentration. This pioneering work paved the way for the development of polypentenamer as a novel chemically recyclable polymer materials which can be not only synthesized, but also depolymerized by the same ruthenium catalyst.

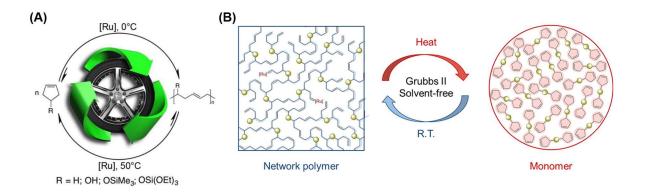


Figure 3. (A) Chemical recycling of polypentenamers bearing siloxy functionalities.⁴¹ (B) Reversible covalent polymer network based on temperature-regulated ROMP and RCMD of functional polypentenamers in the presence of Grubbs 2nd generation catalyst.⁴² Modified and reproduced from ref. 41 and 42 with permission, copyright 2016 and 2018, from the American Chemical Society.

The Tuba group further developed chemically recyclable tire additives based on siloxy functional polypentenamers which are compatible with silica filler (**Figure 3A**).⁴¹ Computational study revealed that the introduction of functional groups on the cyclopentene had a noticeable impact on the ring strain energy and thus the equilibrium monomer concentration. Interestingly, the ring strain energies of trialkoxy silane (i.e., (MeO)₃SiO- and (EtO₃)SiO-) functionalized cyclopentene monomers (7.31 and 6.89 kcal/mol) are relatively higher than that of unmodified cyclopentene (5.44 kcal/mol), resulting in an enhanced activity in ruthenium-catalyzed ROMP. On the other hand, trimethyl silane (Me₃SiO-) functionalized cyclopentene has a markedly lower RSE (3.24 kcal/mol) in comparison to the unmodified one, suggesting that a bulk polymerization condition would be required to achieve high monomer conversions. Importantly, a proof-of-concept study on depolymerization of isolated polypentenamer was conducted, showing a full monomer recovery within 4 min at room temperature when utilizing Hoveyda-Grubbs 2nd generation catalyst (HG2) under highly dilute conditions (i.e., 5 w/v% polymer concentration).

To facilitate depolymerization in a solvent-free or bulk condition which is considered economical and environmentally friendly, Moore et al. studied the role of bulky substituents on the ceiling temperature of functional polypentenamers.⁴² Based on their results, incorporating bulky substituents such as -OR, -COOR, and -CH₂OR on cyclopentene reduced the ring strain energies and led to tunable ceiling temperatures ranging from 50 to 100 °C, which were significantly lower than that of unmodified polypentenamer ($T_{c,neat}$ = 185 °C). The depolymerization-repolymerization cycle was reversible in the presence of Grubbs 2nd generation catalyst for multiple cycles. Initial polymerization of cyclopentene bearing a COOBn group at 25 °C resulted in a 51% monomer conversion and a polymer with 41 kDa. After heating at 50 °C, depolymerization was predominant, decreasing the monomer conversion to 13%, and the polymer molecular weight to 2.1 kDa. Moreover, those monofunctional cyclopentene monomers and bifunctional crosslinkers were copolymerized to construct reversible covalent polymer networks capable of transitioning

between a stiff solid and a liquid state for several cycles by simply varying the temperatures (**Figure 3B**). Rheological test revealed that the recovery of storage modulus upon repolymerization can be improved to 60% by lowering the depolymerization temperature via copolymerization.

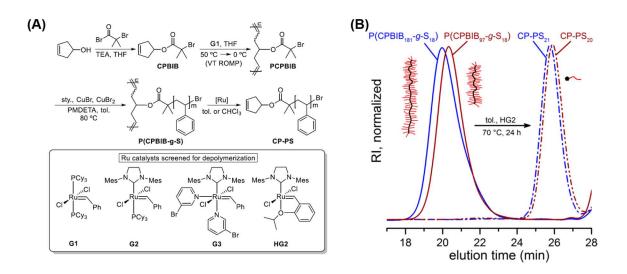


Figure 4. (A) Synthesis of bottle brush polypentenamers and their depolymerization. (B) SEC analysis of bottle brush polypentenamers before and after the depolymerization in the presence of HG2. Modified and reproduced from ref. 39 with permission, copyright 2019, from the American Chemical Society.

Kennemur and coworkers further extended the scope of RCMD in bottle brush polypentenamers, uncovering the different depolymerization pathways for bottle brush and linear polypentenamers.³⁹ The bottle brush polypentenamers were synthesized by variable temperature ROMP of cyclopentene bearing a bromoisobutyryl group (CPBIB), and subsequent atom transfer radical polymerization of styrene, giving rise to the polypentenamer backbone and polystyrene side chains (**Figure 4A**). A quantitative depolymerization of resulting bottle brush polypentenamers was observed at 70°C in toluene after 24 h by applying HG2 catalyst (**Figure 4B**). In contrast to linear polypentenamers which depolymerized in a random fashion, the bottle brush polypentenamer underwent an end-to-end depolymerization, as suggested by the size

exclusion chromatography (SEC) analysis. To investigate the catalyst effect, depolymerization of bottle brush polypentenamer was conducted using different metathesis catalysts including Grubbs 1st generation (G1), 2nd generation (G2), 3rd generation (G3), and HG2 under the same conditions. Based on depolymerization kinetic study, G1, G2, and G3 depolymerize the bottle brush polypentenamers significantly faster than HG2, which could be potentially explained by the boomerang mechanism involving HG2. Notably, the depolymerized cyclopentene-polystyrene macromonomer can undergo macromolecular metamorphosis into star polymers via radical thiolene chemistry.

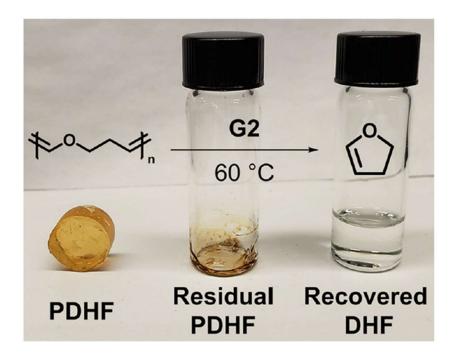


Figure 5. Bulk depolymerization of poly(2,3-dihydrofuran) in the presence of G2 catalyst. Modified and reproduced from ref. 34 with permission, copyright 2020, from the American Chemical Society.

Beyond cyclopentene-based monomers, a set of five-membered heterocyclic monomers have been recently exploited for preparing novel depolymerizable polyolefins.^{34, 43, 44} Xia et al. reported an effective ROMP of 2,3-dihydrofuran (DHF), which is a biomass-derived cyclic enol ether with a low RSE (5.0 kcal/mol).³⁴ In their study, neat DHF was polymerized in the presence of G2 and

chain transfer agent under an ambient atmosphere, leading to polyDHF with tunable molecular weights ranging from 0.29 to 127.7 kDa. The resulting polyDHF materials exhibited a rubbery state with a glass transition temperature of -50 °C and thermal stability up to 320 °C. Most importantly, the solid-state polyDHF was capable of undergoing solvent-free depolymerization into original DHF monomer at 60 °C using G2 catalyst, suggesting its potential as chemically recyclable elastomers (**Figure 5**).

Very recently, the Wang group demonstrated the mechanochemical generation of poly(2,5-dihydrofuran), a depolymerizable polyolefin with a low T_c .⁴³ Prior to this creative study, the traditional ROMP synthesis of poly(2,5-dihydrofuran) was rather challenging due to the very low RSE of 2,5-dihydrofuran (3.4 kcal/mol). Indeed, G3-catalyzed ROMP of 2,5-dihydrofuran in bulk resulted in only 23% monomer conversion.⁴³ To address this synthetic challenge, Wang and coworkers designed and synthesized a novel monomer containing a cyclobutene-fused tetrahydrofuran and two -CH₂-O-CH₂- spacers that connect the cyclobutane and an alkene. The fused-ring monomer has a relatively high RSE (7.9 kcal/mol), facilitating its ROMP into a high T_c polyolefin which exhibited a T_g of -17 °C and a decomposition temperature of 332 °C. Further, mechanochemical activation of the resulting polymer led to ring-opening of cyclobutane, and concomitant formation of poly(2,5-dihydrofuran) up to 68% in the copolymer structure. According to the kinetic study on G3-triggered depolymerization at 30 °C, 33% of poly(2,5-dihydrofuran) segment was depolymerized after 5min, and a complete depolymerization was observed at 2 h in a dilute solution. Notably, the mechanical property of crosslinked polymer film was evaluated by uniaxial compression testing, showing Young's modulus of 1.03 ± 0.19 MPa.

A novel class of enyne self-immolative polymer (SIP) capable of metathesis cascade-triggered depolymerization was recently developed by the Niu group.⁴⁴ In this work, a 1,6-enyne motif with the *p*-pentyl-*N*-benzenesulfonamide spacer was designed and identified as the optimal backbone structure for the SIPs. Either polycondensation or iterative exponential growth approach was

adopted for the synthesis of SIPs. Notably, the resulting SIPs rapidly depolymerized into the low strain five-membered 3,3'-bidihydropyrrole derivatives within 30 min at room temperature when G3 was applied, highlighting their potential as stimuli-responsive materials for controlled release of heterocyclic reagents.

3. Depolymerizable Polyolefins Based on Six-Membered Cyclic Monomers

Compared to five-membered cyclic monomers, the ring strain energy of six-membered cyclohexene is markedly smaller (~ 2.5 kcal/mol), making it non-polymerizable under standard ROMP conditions. Despite the inertness of cyclohexene in ROMP, recent studies have shown that a rational design of cyclohexene derivatives by converting cyclohexene into fused ring monomers would increase their RSEs to an adequate level, making them active in both ROMP and RCMD. 45, 46

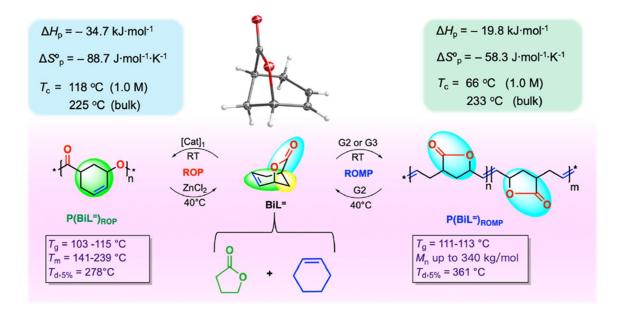


Figure 6. Fused-ring strategy to increase the RSE of cyclohexene-based monomer, thus enabling its ROMP and RCMD. Modified and reproduced from ref. 46 with permission, copyright 2022, from the American Chemical Society.

In 2022, Chen and coworkers demonstrated a bicyclic monomer that hybridized two difficult-to-polymerize rings including cyclohexene and γ -butyrolactone, giving rise to an increase in the RSEs of both cyclohexene and lactone moieties (**Figure 6**).⁴⁶ This hybrid monomer can be polymerized orthogonally between ring-opening polymerization (ROP) and ring-opening metathesis polymerization, affording two polymers (i.e., polyester via ROP, and polyolefin via ROMP). The resulting polyolefin exhibited a high glass transition temperature (T_g = 111-113 °C) and an exceptional thermal stability up to 361 °C. Dynamic mechanical analysis further showed a high storage modulus (1.65 ± 0.13 GPa) for the polyolefin. According to tensile test, the polyolefin material can be defined as a tough and hard plastic which was highlighted by a high Young's modulus (3.8 ± 0.6 GPa), a high ultimate tensile strength (40.0 ± 10.9 MPa), and a modest elongation at break (76 ± 9%). Remarkably, both polyester and polyolefin exhibited full chemical recyclability under mild conditions (25–40 °C) in the presence of a catalyst, closing the one monomer-two polymers-one monomer loop. In particular, the depolymerizable polyolefin can undergo RCMD with 0.1 mol % loading of G2 at 40 °C, recovering the original monomer in 93% yield.

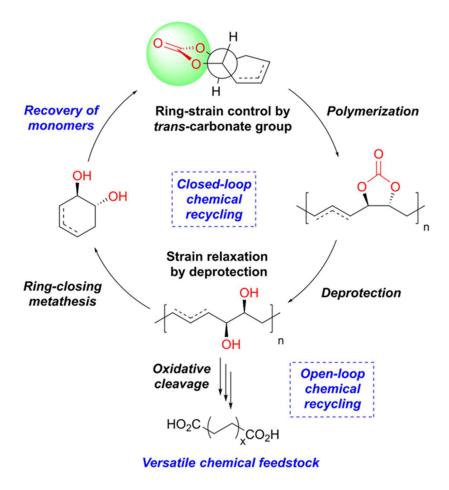


Figure 7. Chemical recycling of oxygen-enriched poly(cyclohexene)s via (*i*) ROMP of *trans*-carbonate-fused cyclohexene monomers, (*ii*) deprotection, (*iii*) RCMD of diol-containing poly(cyclohexene), and (*iv*) regeneration of *trans*-carbonate-fused cyclohexene monomers. Modified and reproduced from ref. 45 with permission, copyright 2023, from the Cell Press.

Very recently, Hong et al. reported the ROMP of *trans*-carbonate-fused cyclohexene monomers to produce oxygen-enriched chemically recyclable polyolefins (**Figure 7**).⁴⁵ In their study, the low-strain and non-polymerizable vicinal *trans*-cyclohexene-diols (RSEs = 1.92–2.14 kcal/mol) were transformed into two *trans*-carbonate-fused cyclohexene monomers with relatively higher RSEs (6.0 and 10.3 kcal/mol), which can be polymerized by living ROMP using G3. The two resulting carbonate polymers showed high thermal stability over 310 °C, and glass transition temperatures of 62, and 79 °C, respectively. The base-promoted hydrolysis of carbonate polymers gave rise to

hydroxyl-group-enriched poly(cyclohexene)s with a well-defined 1,2-diol structure in every repeat unit. Because of the low strain of vicinal trans-cyclohexene-diols, the hydroxy-functional poly(cyclohexene) can be efficiently depolymerized back to vicinal trans-cyclohexene-diols by ring-closing metathesis depolymerization in the presence of G2 catalyst, demonstrating a closed-loop recycling of functional poly(cyclohexene)s. Moreover, the mechanical properties of hydrogenated hydroxy-functional polymer were evaluated, exhibiting a tensile strength of 27.7 MPa with an elongation at break of around 95% which are similar to commonly used packaging materials such as low-density polyethylene (LDPE). Notably, the researchers also developed an open-loop recycling strategy by performing oxidative cleavage of the 1,2-diol groups of the polymers, leading to the production of industrially useful α, ω -dicarboxylic acids.

Capitalizing on the low RSEs of cyclohexene and cyclopentene, the Jones lab developed a clever synthetic approach to depolymerizable polyurethanes.⁴⁷ They began the study by designing two diol monomers which contain unsaturated alkenes in a configuration favoring ring-closing metathesis to cyclohexene and cyclopentene derivatives. These diol monomers were incorporated into the polymer backbone by their polycondensation with diisocyanates and triisocyanates, generating linear and crosslinked polyurethanes, respectively. The resulting polyurethanes can be fully depolymerized in solution upon exposure to HG2 catalyst, leading to cyclohexene or cyclopentene-containing products with low molecular weight (< 500 g/mol). While the depolymerization did not regenerate the original monomers, the chemical recyclability of depolymerized products was demonstrated by their repolymerization through free-radical polymerization or radical thiol-ene reaction.

4. Depolymerizable Polyolefins Based on Eight-Membered Cyclic Monomers

Despite the promise in chemical recycling of five-membered cyclic olefin monomers such as cyclopentene derivatives and DHF, their homopolymers exhibit T_g values below or near room temperature, limiting the scope of their industrial use. To promote the development of chemically

recyclable polyolefins with tunable thermomechanical properties for a broader range of applications, the Wang group recently invented a novel class of depolymerizable polyolefins based on a series of fused-ring cyclooctene monomers including *trans*-cyclobutane-fused cyclooctene (*t*CBCO), *trans*-cyclopentane-fused cyclooctene (*t*CPCO), and *trans*-five-membered cyclic acetal-fused cyclooctene (*t*CACO). 19, 48-52

In their seminal work, Wang and coworkers first investigated the effect of fused rings on the ring strain energy of cyclooctene. 19 According to computational analysis, the incorporation of a trans-fused cyclobutane at the 5 and 6 positions lowered the RSE of cyclooctene from 8.2 kcal/ mol in its original form to 4.9 kcal/mol in the fused ring, which is comparable to that of cyclopentene and thus should facilitate depolymerization of the corresponding polymer. Therefore, trans-cyclobutane-fused cyclooctene was identified as an ideal monomer system for the preparation of depolymerizable polyolefins. Moreover, UV-induced isomerization of tCBCO monomers led to their highly strained E-isomers, enabling the synthesis of well-defined poly(tCBCO)s via controlled ROMP. Depolymerization of the resulting poly(tCBCO)s triggered by G2 at concentrations below 200 mM showed a substantial recovery of original tCBCO monomers (94-98%). However, further increasing the concentration above 200 mM resulted in lower depolymerization conversions. It is noteworthy to mention that a wide range of glass transition temperatures (from -30 °C to 100 °C) was accessed through functionalization of the tCBCO monomers, suggesting the potential applications of poly(tCBCO)s as elastomers and plastics. For instance, tensile test of imide-functional tCBCO polymer showed a Young's modulus of 1.40 ± 0.06 GPa, a tensile strength of 39 \pm 5 MPa, and a strain at break around 3.4 \pm 0.3%, which are comparable to those of commercial polystyrene.

To further understand how the substituents on cyclobutane govern the thermodynamic and thermal properties of poly(tCBCO)s, the Wang group designed a series of tCBCO monomers with different stereochemistry of ester substituents on the cyclobutane, and monomers with additional

methyl and cyclohexyl substituents.⁵⁰ All those monomers underwent ROMP to produce high molecular weight polymers (> 80 kDa) with molecular weight distributions ranging from 1.6 to 2.1. Differential scanning calorimetry (DSC) analysis revealed significant variations in the T_g values among the resulting polymers. Interestingly, the polymer with *trans*-ester groups on the cyclobutane exhibited a T_g of -1°C, which was 19 °C lower than their *cis*-isomer. Moreover, the T_g values for poly(tCBCO)s containing methyl and cyclohexane substituents were determined to be 50°C, and 61°C, respectively. Depolymerization study was performed at various olefin concentrations in the presence of G2. Under dilute conditions (< 200 mM), a significant extent of depolymerization exceeding 90% was observed in all the polymers. As the concentration was increased to 400 mM, the investigated polymers displayed noticeably different depolymerizability, with the highest depolymerization extent (87%) found for the poly(tCBCO) with *cis*-ester groups. Collectively, these results demonstrated that the thermodynamics and thermal properties of poly(tCBCO)s can be tuned by relatively small structural changes, providing fundamental insights into the design of chemically recyclable polymer materials.

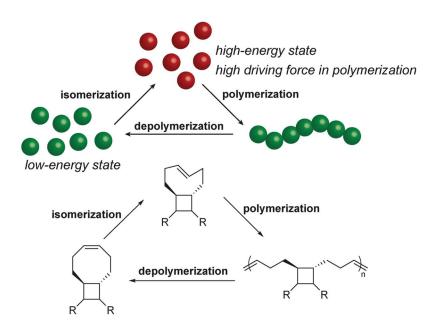


Figure 8. Chemical recycling of poly(*t*CBCO)s via (*i*) monomer isomerization, (*ii*) living ring-opening metathesis polymerization, and (*iii*) ring-closing metathesis depolymerization. Light-

induced *cis*-to-*trans* alkene isomerization of *t*CBCO monomers significantly increases the ring strain energy, enabling the living ROMP process. Modified and reproduced from ref. 48 with permission, copyright 2021, from Wiley-VCH GmbH.

In a follow-up study led by the same group, photoinduced cis-to-trans alkene isomerization of tCBCO was leveraged to increase the driving force in the forward polymerization (Figure 8).48 The photoisomerization efficiency was significantly improved by adopting a flow photochemistry method, leading to satisfactory yields of the highly strained E-alkene tCBCO monomers (30-81%). The researchers further investigated the effects of catalyst type and triphenylphosphine (PPh₃) ligand on the polymerization behaviors of E-alkene tCBCOs. Based on the catalyst screening result, a combination of G1 catalyst and an excess of PPh3 not only suppressed the secondary metathesis events, but also significantly diminished the depolymerization, as evidenced by the high monomer conversion (>97%) and low dispersity of the resulting polymer. The excess PPh₃ competes with the monomers for the ruthenium center, leading to a low concentration of active catalyst which would diminish the undesired inter- and intramolecular chain transfer events.⁵³ To demonstrate the living ROMP feature enabled by the E-alkene tCBCO monomers, block copolymer synthesis was attempted and successfully achieved by sequential addition of two different E-alkene tCBCO monomers. The resulting diblock copolymer showed two distinct glass transition temperatures at -31 and 88 °C, which are in good agreement with the $T_{\rm g}$ values of respective homopolymers. Notably, the isolated block copolymers were fully depolymerizable under dilute conditions (25 mM of olefin) in the presence of 1mol% G1 or G2.

By applying the *t*CBCO chemistry, Wang and colleagues recently introduced a novel class of chemically recyclable semi-fluorinated polymers with adjustable glass transition temperatures ranging from -2°C to 88°C.⁵² All these polymers exhibited exceptional thermal stability, with decomposition temperatures above 280 °C. Moreover, the hydrophobicity of semi-fluorinated polymers was harnessed to construct block copolymer micelles with a size of 88 nm in water. To

diversify the functionalities of fluorinated polymers, post-polymerization functionalization of poly(*t*CBCO)s bearing pentafluorophenyl imide substituents was achieved via an efficient regioselective *para*-fluoro-thiol substitution reaction. Importantly, *t*CBCO-based semi-fluorinated polymers developed in this study were able to quantitatively depolymerize back into original monomers in the presence of G2, offering a promising solution to a circular economy of fluorinated polymers.

Graft polymers possess unique characteristics useful for a broad range of applications. Nevertheless, the examples of chemically recyclable graft polymers remain rare. To achieve a circular economy of graft polymers, Wang and coworkers leveraged their tCBCO system in preparing well-defined and depolymerizable graft polyolefins with controllable architecture and size.⁵¹ In this study, a "grafting-through" strategy was enabled by living ROMP of the highly strained E-alkene tCBCO macromonomers bearing a side chain such as poly(ethylene glycol), polylactide, and aliphatic chain. The resulting graft polymers were further examined for their depolymerization behaviors under dilute conditions (10 mM of olefin) using 1 mol% G2 catalyst. As expected, tCBCO-based graft polymers completely disintegrated into the low-strain Z-alkene tCBCO macromonomers, which can be further isomerized to E-alkene tCBCO for repolymerization. In addition, the depolymerization kinetics was monitored by SEC which suggested an end-to-end unzipping mechanism, in good agreement with the depolymerization pathway of bottle brush polypentenamers observed by Kennemur. 39 Tensile test of thermoplastic graft copolymer further revealed a Young's modulus of 130 ± 18 MPa, a yield stress of 4.4 ± 0.4 MPa, and a stress at break $(8.5 \pm 0.3 \text{ MPa})$. These mechanical properties are similar to those of LDPE.

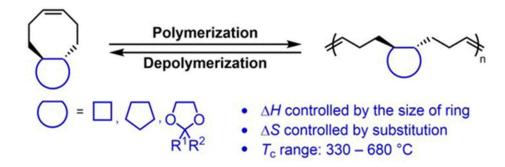


Figure 9. Depolymerizable polyolefins based on a library of fused-ring cyclooctene monomers including *trans*-cyclobutane-fused cyclooctene (*t*CBCO), *trans*-cyclopentane-fused cyclooctene (*t*CPCO), and *trans*-five-membered cyclic acetal-fused cyclooctene (*t*CACO). Modified and reproduced from ref. 49 with permission, copyright 2022, from the American Chemical Society.

To better understand the relationship between monomer structure and polymerization thermodynamics, Wang and coworkers recently expanded the scope of fused-ring cyclooctenes to a series of monomers including *t*CBCOs, *t*CPCOs, and *t*CACOs (**Figure 9**). ⁴⁹ Density functional theory revealed that all those four-membered and five-membered rings *trans*-fused to cyclooctene lowered the RSEs of monomer, resulting in a narrow range of enthalpy change from -2.1 to -3.3 kcal/mol at 1.0 M. While the range of enthalpy change was narrow, the ceiling temperatures at 1.0 M differed by a span of 340 °C, thanks to the low entropy changes from -2.7 to -5.0 cal/mol/k. Notably, even though the geminal substituents on the *t*CACOs are not directly attached to the cyclooctene ring, they managed to reduce the *T*_c by 300°C, allowing for a promoted depolymerization of the corresponding polyolefins. Moreover, the researchers claimed that the synthesis of *t*CACO monomers is more facile and scalable compared to *t*CBCOs, making them attractive building blocks for producing chemically recyclable polyolefins.

Recently, Lemcoff and coworkers developed a *cis*-diiodo sulfur chelated ruthenium benzylidene catalyst (Ru-S-I) that can trigger the depolymerization of commercial *cis*-1,4-polybutadiene into small cyclic olefins including 1,5-cyclooctadiene (COD).⁵⁴ According to their study, Ru-S-I was not reactive to internal olefins such as polybutadiene due to the steric hindrance.

However, when a small amount of terminal olefin substrate was added, the depolymerization of polybutadiene readily occurred in the presence of Ru-S-I. While the yield of COD was low, the ability of Ru-S-I to depolymerize polybutadiene into its pristine monomer suggested its potential for chemical recycling of industrially important polymer (i.e., polybutadiene).

5. Depolymerizable Polyolefins Based on Macrocyclic Monomers

Beyond low-strain small sized ring monomers (i.e., 5-, 6-, and 8-membered), the strainless macrocyclic olefins have also been utilized for the synthesis of depolymerizable polyolefins. ⁵⁵⁻⁵⁷ In 1997, Grubbs et al. reported the equilibrium ROMP of unsaturated crown ether monomers with ring sizes of 14 and 17. ⁵⁶ In their pioneering work, the macrocyclic crown ether monomers were synthesized via template-directed ring-closing metathesis of oligoethylene glycol dienes in the presence of an alkali metal ion template such as Li⁺. The presence of template can preemptively organize the dienes through noncovalent interactions, providing the conformational restrictions to facilitate the RCM process (**Figure 10A**). Furthermore, ROMP of the macrocyclic monomers with G1 catalyst was achieved at high monomer concentration (1.1 M), leading to polyolefins analogous to polyethylene glycol. Importantly, the resulting polymer can quantitatively depolymerize back to the original macrocyclic monomers under dilute solutions (50 mM) in the presence of template. When the template was absent, depolymerization gave rise to a low yield of monomers (~20%), with the majority of depolymerized products identified as low molecular weight polymer.

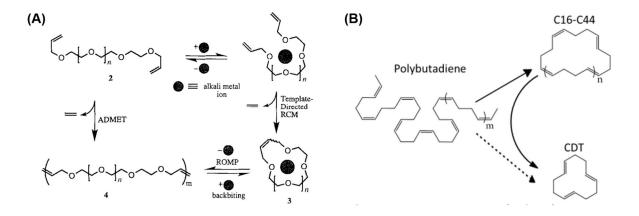


Figure 10. (A) Template-directed RCM synthesis of macrocyclic crown ether monomers and their equilibrium ROMP.⁵⁶ (B) Chemical upcycling of commercial 1,4-polybutadiene into high-value macrocyclic oligo(butadiene)s.⁵⁵ Modified and reproduced from ref. 56 and 55 with permission, copyright 1997 and 2016, from Wiley-VCH GmbH and the Royal Society of Chemistry, respectively.

Hodge and coworkers demonstrated the cyclo-depolymerization of olefin-containing polyesters to generate large unstrained macrocyclic olefins with ring sizes ranging from 21 to 84.⁵⁷ The researchers harnessed acyclic diene metathesis polymerization technique to prepare the olefin-containing polyesters. Two metathesis catalysts including G1 and G2 were screened for their performance in depolymerization. It was found that G2 completed the depolymerization in 2-4 h, significantly faster than G1-catalyzed depolymerization that required several days. It is worth mentioning that the depolymerization led to a mixture of macrocycles, which can be efficiently separated by SEC column. To evaluate the feasibility of closed-loop recycling, the as-synthesized macrocyclic olefins were further examined for their ROMP activity. It was observed that all those monomers successfully underwent entropy-driven ROMP under neat or very concentrated solutions, producing high molecular weight polyolefins with broad molecular weight distributions.

Large macrocycles consisting of butadiene subunits (C16-44) are valuable building blocks due to their unique physicochemical properties such as low viscosity, high thermal stability, and multi-

unsaturation.⁵⁸ However, traditional synthetic protocols for such cyclic oligo(butadiene)s are unscalable and expensive. To develop a robust synthetic approach to large cyclic oligo(butadiene)s, the Sels group investigated the cyclo-depolymerization of commercial 1,4-polybutadiene in the presence of Ru catalyst.⁵⁵ According to their study, high molecular weight 1,4-polybutadiene with a low content of vinyl groups can be efficiently depolymerized into macrocyclic oligo(butadiene)s under dilute conditions (< 0.3 M of butadiene units). Kinetic study of the depolymerization revealed a two-step mechanism, involving an initial backbiting of polybutadiene to large macrocycles (C16-44), followed by their conversions into thermodynamically favored 12-membered *t,t,t*-cyclododecatriene (CDT) via tandem ring-opening/ring closing metathesis (**Figure 10B**). Interestingly, the distribution of macrocyclic products was dependent on the ligand structure of the Ru catalyst. While G2 catalyst favored the formation of undesired CDT, the relatively less active G1 can selectively depolymerize polybutadiene into the C16-44 macrocyclic oligo(butadiene)s. This study provided a promising solution for the chemical upcycling of polybutadiene wastes into valuable products.

6. Conclusion and Future Perspectives

In summary, we have highlighted the recent advances in chemical recycling of polyolefins enabled by ring-closing metathesis depolymerization. To date, four main types of low-strain cyclic olefin monomers including five-membered, six-membered, eight-membered, and macrocycles have been utilized for the synthesis of depolymerizable polyolefins, giving rise to a diverse set of chemically recyclable polymer materials with tunable ceiling temperatures and thermomechanical properties.

Critically, the reported ring strain energies of cyclic olefin monomers or RCM products that facilitate the depolymerization are typically below 5.3 kcal/mol.^{34, 42, 43, 45, 46, 49} Based on this cut-off, a potentially new class of monomers for depolymerizable polyolefins would be the seven-membered cycloheptene derivatives which have a reported RSE of 5.1 kcal/mol.³⁶ In addition, it

should be noted that high RSE monomers which can be converted to low RSE monomers could also be used for the production of depolymerizable polyolefins. For instance, ROMP of highly strained E-alkene *t*CBCO monomers led to well-defined poly(*t*CBCO)s, which were capable of depolymerizing into the low-strain Z-alkene *t*CBCO monomers. In Hong's study, the carbonate-bearing poly(cyclohexene)s synthesized by ROMP of strained *trans*-carbonate-fused cyclohexene monomers can be hydrolyzed into hydroxy-functional poly(cyclohexene)s. The resulting hydroxy-functional polymers were able to depolymerize into low-strain vicinal *trans*-cyclohexene-diols, which can be used for the regeneration of *trans*-carbonate-fused cyclohexene monomers.

It is noteworthy to point out that the polymer concentration plays a pivotal role in the depolymerization process. In the majority of the studies reviewed, depolymerization was performed under dilute conditions which required an appreciable amount of organic solvent, compromising its potential in recycling industry. Only a few low T_g polymers made by volatile monomers such as 2,3-dihydrofuran and cyclopentene have been demonstrated feasible for bulk depolymerization.^{34, 42} Therefore, we envision that future design of new polyolefins capable of solvent-free depolymerization would be highly desired for promoting an economical and scalable recycling protocol.⁹

Last but not least, it is typically tedious to separate or recycle the homogeneous ruthenium catalysts from the RCM products and solvent upon the depolymerization. In light of this, heterogeneous catalysts that immobilize the ruthenium species on the solid support would offer operational and economic advantages over their homogeneous counterparts. ⁵⁹⁻⁶¹ Indeed, various heterogeneous ruthenium catalysts have been proven robust in multiple cycles of RCM synthesis towards small molecule cyclic olefins. ^{60, 61} The application of such recyclable catalysts in ring-closing metathesis depolymerization remains unexplored, but would be expected in the future.

Given the strong motivation for developing more and diversified chemically-recyclable polymers as the next-generation materials, we believe that ring-closing metathesis depolymerization will continue to serve as a powerful strategy towards closed-loop chemical recycling and upcycling of many new polyolefin materials.

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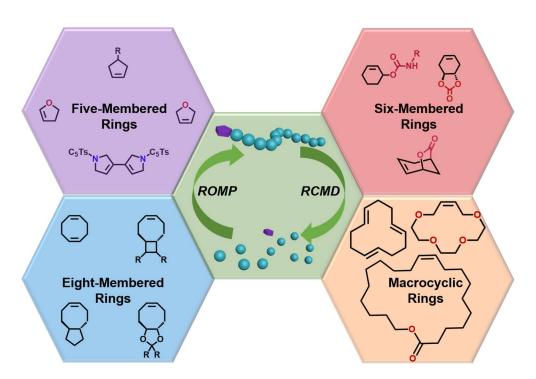
References

- 1. H. Staudinger, Ber. Dtsch. Chem. Ges., 1920, **53**, 1073-1085.
- 2. H. Ringsdorf, Angew. Chem. Int. Ed., 2004, 43, 1064-1076.
- 3. A. S. Abd-El-Aziz, M. Antonietti, C. Barner-Kowollik, W. H. Binder, A. Boker, C. Boyer, M. R. Buchmeiser, S. Z. D. Cheng, F. D'Agosto, G. Floudas, H. Frey, G. Galli, J. Genzer, L. Hartmann, R. Hoogenboom, T. Ishizone, D. L. Kaplan, M. Leclerc, A. Lendlein, B. Liu, T. E. Long, S. Ludwigs, J. F. Lutz, K. Matyjaszewski, M. A. R. Meier, K. Mullen, M. Mullner, B. Rieger, T. P. Russell, D. A. Savin, A. D. Schluter, U. S. Schubert, S. Seiffert, K. Severing, J. B. P. Soares, M. Staffilani, B. S. Sumerlin, Y. M. Sun, B. Z. Tang, C. B. Tang, P. Theato, N. Tirelli, O. K. C. Tsui, M. M. Unterlass, P. Vana, B. Voit, S. Vyazovkin, C. Weder, U. Wiesner, W. Y. Wong, C. Wu, Y. Yagci, J. Y. Yuan and G. Z. Zhang, *Macromol. Chem. Phys.*, 2020, **221**, 2000216.
- 4. Plastics Europe, 2021, https://plasticseurope.org/wp-content/uploads/2021/12/Plastics-the-Facts-2021-web-final.pdf
- 5. T. H. Epps, 3rd, L. T. J. Korley, T. Yan, K. L. Beers and T. M. Burt, *JACS Au*, 2022, **2**, 3-11.
- 6. H. Sun, Y. Liang, M. P. Thompson and N. C. Gianneschi, *Prog. Polym. Sci.*, 2021, **120**, 101427.
- 7. R. C. Thompson, C. J. Moore, F. S. vom Saal and S. H. Swan, *Philos. Trans. R. Soc. B*, 2009, **364**, 2153-2166.
- 8. I. Vollmer, M. J. F. Jenks, M. C. P. Roelands, R. J. White, T. van Harmelen, P. de Wild, G. P. van der Laan, F. Meirer, J. T. F. Keurentjes and B. M. Weckhuysen, *Angew. Chem. Int. Ed.*, 2020, **59**, 15402-15423.
- 9. J. B. Young, R. W. Hughes, A. M. Tamura, L. S. Bailey, K. A. Stewart and B. S. Sumerlin, *Chem*, 2023, **9**, 2669-2682.
- 10. J. B. Young, J. I. Bowman, C. B. Eades, A. J. Wong and B. S. Sumerlin, *ACS Macro Lett.*, 2022, **11**, 1390-1395.
- 11. X. L. Li, R. W. Clarke, H. Y. An, R. R. Gowda, J. Y. Jiang, T. Q. Xu and E. Y. Chen, *Angew. Chem. Int. Ed.*, 2023, **62**, e202303791.
- 12. M. R. Martinez, S. Dadashi-Silab, F. Lorandi, Y. Zhao and K. Matyjaszewski, *Macromolecules*, 2021, **54**, 5526-5538.

- 13. G. R. Jones, H. S. Wang, K. Parkatzidis, R. Whitfield, N. P. Truong and A. Anastasaki, *J. Am. Chem. Soc.*, 2023, **145**, 9898-9915.
- 14. M. Hong and E. Y. X. Chen, *Green Chem*, 2017, **19**, 3692-3706.
- 15. D. J. Lloyd, V. Nikolaou, J. Collins, C. Waldron, A. Anastasaki, S. P. Bassett, S. M. Howdle, A. Blanazs, P. Wilson, K. Kempe and D. M. Haddleton, *Chem Commun*, 2016, **52**, 6533-6536.
- 16. P. Olsen, J. Undin, K. Odelius, H. Keul and A. C. Albertsson, *Biomacromolecules*, 2016, **17**, 3995-4002.
- 17. I. M. Maafa, *Polymers*, 2021, **13**, 225.
- 18. V. K. Soni, G. Singh, B. K. Vijayan, A. Chopra, G. S. Kapur and S. S. V. Ramakumar, *Energy & Fuels*, 2021, **35**, 12763-12808.
- 19. D. Sathe, J. Zhou, H. Chen, H. W. Su, W. Xie, T. G. Hsu, B. R. Schrage, T. Smith, C. J. Ziegler and J. Wang, *Nat. Chem.*, 2021, **13**, 743-750.
- 20. A. Leitgeb, J. Wappel and C. Slugovc, *Polymer*, 2010, **51**, 2927-2946.
- 21. A. Mandal and A. F. M. Kilbinger, ACS Macro Lett., 2023, 12, 1372-1378.
- 22. M. Yasir, P. Liu, I. K. Tennie and A. F. M. Kilbinger, *Nat. Chem.*, 2019, **11**, 488-494.
- 23. K. A. Ogawa, A. E. Goetz and A. J. Boydston, *J. Am. Chem. Soc.*, 2015, **137**, 1400-1403.
- 24. H. Sun, T. Ibrahim, A. Ritacco and K. Durkee, *ACS Macro Lett.*, 2023, **12**, 1642–1647.
- 25. A. Rizzo, E. Jung, H. Song, Y. Cho, G. I. Peterson and T. L. Choi, *J. Am. Chem. Soc.*, 2022, **144**, 15643-15652.
- 26. P. Shieh, H. V. Nguyen and J. A. Johnson, *Nat. Chem.*, 2019, **11**, 1124-1132.
- 27. Y. Liang, H. Sun, W. Cao, M. P. Thompson and N. C. Gianneschi, *ACS Macro Lett.*, 2020, **9**, 1417-1422.
- 28. H. Sun, B. Qiao, W. Choi, N. Hampu, N. C. McCallum, M. P. Thompson, J. Oktawiec, S. Weigand, O. M. Ebrahim, M. O. de la Cruz and N. C. Gianneschi, *ACS Cent. Sci.*, 2021, **7**, 2063-2072.
- 29. W. J. Neary and J. G. Kennemur, *Macromolecules*, 2017, **50**, 4935-4941.
- 30. K. Tashiro, M. Akiyama, K. Kashiwagi and T. Okazoe, *J. Am. Chem. Soc.*, 2023, **145**, 2941-2950.
- 31. G. C. Vougioukalakis and R. H. Grubbs, *Chem. Rev.*, 2009, **110**, 1746-1787.
- 32. B. M. Novak, W. Risse and R. H. Grubbs, *Adv. Polym. Sci.*, 1992, **102**, 47-72.
- 33. U. Frenzel and O. Nuyken, J. Polym. Sci. Part A: Polym. Chem., 2002, 40, 2895-2916.
- 34. J. D. Feist and Y. Xia, J. Am. Chem. Soc., 2020, **142**, 1186-1189.
- 35. M. Hong and E. Y. X. Chen, *Nat. Chem.*, 2016, **8**, 42-49.
- 36. A. Hlil, J. Balogh, S. Moncho, H. Su, R. Tuba, E. N. Brothers, M. Al-Hashimi and H. S. Bazzi, *J. Polym. Sci. Part A: Polym. Chem.*, 2017, **55**, 3137-3145.
- 37. B. Lebedev, N. y. Smirnova, Y. Kiparisova and K. Makovetsky, *Makromol. Chem.*, 1992, **193**, 1399-1411.
- 38. R. Tuba and R. H. Grubbs, *Polym. Chem.*, 2013, **4**, 3959-3962.
- 39. W. J. Neary, T. A. Isais and J. G. Kennemur, J. Am. Chem. Soc., 2019, **141**, 14220-14229.
- 40. W. J. Neary and J. G. Kennemur, ACS Macro Lett., 2019, **8**, 46-56.
- 41. R. Tuba, J. Balogh, A. Hlil, M. Barlog, M. Al-Hashimi and H. S. Bazzi, *ACS Sustain. Chem. Eng.*, 2016, **4**, 6090-6094.
- 42. H. Liu, A. Z. Nelson, Y. Ren, K. Yang, R. H. Ewoldt and J. S. Moore, *ACS Macro Lett.*, 2018, **7**, 933-937.
- 43. T. G. Hsu, S. Liu, X. Guan, S. Yoon, J. Zhou, W. Y. Chen, S. Gaire, J. Seylar, H. Chen, Z. Wang, J. Rivera, L. Wu, C. J. Ziegler, R. McKenzie and J. Wang, *Nat. Commun.*, 2023, **14**, 225.
- 44. J. Yuan, G. J. Giardino and J. Niu, *Angew. Chem. Int. Ed.*, 2021, **60**, 24800-24805.
- 45. K. Choi and S. H. Hong, *Chem*, 2023, **9**, 2637-2654.
- 46. C. Shi, R. W. Clarke, M. L. McGraw and E. Y. Chen, *J. Am. Chem. Soc.*, 2022, **144**, 2264-2275.

- 47. B. H. Jones, C. Staiger, J. Powers, J. A. Herman and J. Roman-Kustas, *Macromol. Rapid. Commun.*, 2021, **42**, e2000571.
- 48. H. Chen, Z. Shi, T. G. Hsu and J. Wang, *Angew. Chem. Int. Ed.*, 2021, **60**, 25493-25498.
- 49. J. Zhou, D. Sathe and J. Wang, J. Am. Chem. Soc., 2022, **144**, 928-934.
- 50. D. Sathe, H. Chen and J. Wang, *Macromol. Rapid. Commun.*, 2023, **44**, e2200304.
- 51. Z. Wang, S. Yoon and J. Wang, *Macromolecules*, 2022, **55**, 9249-9256.
- 52. D. Sathe, J. Zhou, H. Chen, B. R. Schrage, S. Yoon, Z. Wang, C. J. Ziegler and J. Wang, *Polym. Chem.*, 2022, **13**, 2608-2614.
- 53. R. Walker, R. M. Conrad and R. H. Grubbs, *Macromolecules*, 2009, **42**, 599-605.
- 54. N. B. Nechmad, R. Phatake, E. Ivry, A. Poater and N. G. Lemcoff, *Angew. Chem. Int. Ed.*, 2020, **59**, 3539-3543.
- 55. A. Dewaele, T. Renders, B. Yu, F. Verpoort and B. F. Sels, *Catal. Sci. Technol.*, 2016, **6**, 7708-7717.
- 56. M. J. Marsella, H. D. Maynard and R. H. Grubbs, *Angew. Chem. Int. Ed.*, 1997, **36**, 1101-1103.
- 57. S. D. Kamau, P. Hodge, A. J. Hall, S. Dad and A. Ben-Haida, *Polymer*, 2007, **48**, 6808-6822.
- 58. Z. Jia and M. J. Mnnteiro, *J. Polym. Sci. Part A: Polym. Chem.*, 2012, **50**, 2085-2097.
- 59. C. Che, W. Li, S. Lin, J. Chen, J. Zheng, J. Wu, Q. Zheng, G. Zhang, Z. Yang and B. Jiang, *Chem. Commun.*, 2009, 5990-5992.
- 60. L. Xia, T. Peng, G. Wang, X. Wen, S. Zhang and L. Wang, ChemistryOpen, 2019, 8, 45-48.
- 61. S. T. Nguyen and R. H. Grubbs, J. Organomet. Chem., 1995, 497, 195-200.

Table of Content Graphic



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