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Sustainable high-density polyethylene via chemical recycling: From modification to polymerization methods

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ABSTRACT

High-density polyethylene (HDPE) is among the most voluminous commodity plastic, which has received increasing public scrutiny about its impact on environment and climate change. There have been many efforts to recycle HDPE chemically, though significant hurdles remain. Toward a closed-loop economy, it is considered appealing to design "HDPE-like" materials, which contain built-in degradable groups and preserve thermal and mechanical properties like HDPE. This review provides a concise overview of three major areas: HDPE recycling methods, preparation of "HDPE-like" materials, and perspective towards more sustainable polymers. Each section includes a few inspiring achievements and challenges of the past decade.

1. Introduction

The advent of plastic in the 1950s was a boon for mankind because of its incredibly versatile functions and applications in daily routines. Since its invention, plastic products have skyrocketed due to their affordability, durability, light weight, resistance to corrosion, electric insulation, and processability [1]. Based on the projection of the Organisation for Economic Cooperation and Development (OECD) [2], the overall usage of plastic from 2009 to 2019 has risen two-fold, with a total consumption of 460 million tons (Mt) in 2019. There are various types of commodity plastic, each possessing distinct properties that are suitable for specific applications. The packaging industry constitutes the largest plastic usage, accounting for 31 % with a market size exceeding 265 billion U.S. dollars in 2022 [3]. Polyolefins have a significant impact on plastic industry, with a market value exceeding 243 billion U.S. dollars in 2022 and a compound annual growth rate (CAGR) of 5.1 % from 2023 to 2030 [4]. The largest market share in the polyolefin industry is held by two types: polyethylene (PE) and polypropylene (PP). Polypropylene (PP) and low-density polyethylene (LDPE) comprise 17 % and 16 % of global plastic production, respectively. High-density polyethylene (HDPE) follows at 13 %.

The production of HDPE totaled 40 million tons in 2022 with a CAGR of 5.15 % expected till 2035 [5]. The versatility of HDPE is responsible for its widespread use across different sectors. The exceptional mechanical properties and low weight of HDPE make it an attractive commodity with increasing demand for manufacturing lightweight vehicles and construction industry. However, the frequent use of plastic produces a significant amount of waste that possesses severe threats to the environment. Among about 400 million metric tons of plastic produced, over 90 % was discarded as waste [6,7], which includes 50 % stayed in the landfill and 22 % disposed to or leaked to the environment. This allows durable plastic to remain in the environment and degrade into microparticles or nanoparticles causing severe threat to the ecosystem [8]. Given the haunting challenges, there have been tremendous opportunities in developing diverse approaches to designing more sustainable polymers [9–13], including HDPE.

This review article starts with a brief introduction of general methods of recycling plastic, followed by chemical recycling of HDPE. The focus will be on the synthesis of "HDPE-like" polymers, which could shed light on the next generation plastic to replace traditional HDPE.

2. General recycling methods

Recycling plastic has become a crucial measure to safeguard the environment. Different techniques have been developed to recycle various types of plastic, depending on the quality of the recycled materials, the type of plastic, and economic considerations. According to ASTM D7209-06 and ISO 15,270 standards plastic recycling is categorized into four types: primary (closed-loop), secondary (mechanical), tertiary (chemical), and quaternary (energy recovery), as shown in Fig. 1

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[14–16].

Primary and secondary recycling methods use mechanical recycling techniques. However, they differ in terms of the feedstock used. Primary recycling utilizes post-production plastic waste, which is used in similar high-value applications. On the other hand, secondary recycling uses post-consumer plastic waste as feedstock. However, the properties of the plastic can deteriorate due to continuous polymer degradation during each cycle of melt processing and the risk of contamination [15].

Tertiary recycling, also known as chemical recycling, involves modifying the chemical structure of polymers to transform them into either monomers or new raw chemicals. This method is generally used for polymers that are no longer suitable for mechanical recycling [16]. Several technologies, including pyrolysis (cracking), depolymerization (thermal or catalytic), gasification, and solvolysis, have been deployed for the chemical recycling of plastic. However, the solvolysis technique is limited to O- and N-linked polymers such as polyethylene terephthalate, polyamides, and polyurethanes [15]. Tertiary recycling requires advanced infrastructures and could be expensive, making it less common compared to primary and secondary recycling methods. The tertiary recycling will be further detailed in the next section of this article.

Quaternary recycling is a process of plastic waste incineration used for energy recovery. This has become the default method for plastic that is unsuitable for any other type of recycling [17]. Quaternary recycling is in general a more efficient method for large scale waste plastic treatment in comparison to other three recycling methods. However, incineration of the plastic releases noxious and large amounts of greenhouse gases, which is now considered not environmentally feasible [18].

3. Chemical recycling

Chemical recycling, known as depolymerization to monomers or pyrolysis to chemicals, can offer an alternative solution for producing new chemical products or plastic when other recycling methods are not worth considering. A commonly used plastic, polyethylene, is particularly challenging to recycle chemically due to the lack of cleavable functional groups. Conversely, it is more promising for polyethylene to convert into value-added chemicals or materials via chemical upcycling, considering corresponding environmental and economic impacts. It is worthy to mention that the term "upcycling" might be controversial, unless rigorous techno-economic analysis and life-cycle analysis are evaluated, which is beyond the scope of this review. This section briefly addresses conventional chemical recycling methods (pyrolysis and gasification), primarily focusing on HDPE upcycling (catalytic hydroconversion and tandem strategies) and downstream products, as shown in Fig. 2. It is worth mentioning that there are several comprehensive reviews covering a range of chemical recycling and upcycling for polyolefins [8,14,19–23].

3.1. Traditional chemical recycling

Chemical recycling of polyolefins is mostly limited to thermal deconstruction such as pyrolysis and gasification, which typically work at high temperature [24] and can convert the polymers into gaseous (syngas) [25,26] or liquid (aliphatic) [27] chemicals. These processes require a significant amount of energy due to the inert carbon backbone, resulting in low-value products that downgrade the polymers, as shown in Fig. 2.

3.2. Catalytic hydroconversion methods

Polyolefin hydroconversion is an emerging alternative for converting polyolefins into fuels, lubricants, and waxes. This process uses hydrocracking and hydrogenolysis methods to degrade polyolefin chains at moderate temperature, under an atmosphere of hydrogen and a catalyst. The process targets liquid hydrocarbons instead of methane and gaseous alkanes. Several review articles have recently summarized the recycling of polyolefins using catalytic hydroconversion strategies [20,28–30].

3.2.1. Hydrocracking

The hydrocracking process converts heavy plastic into lighter molecules in the presence of hydrogen. It involves dehydrogenation of the polymer backbone, skeletal rearrangement, cleavage of carbon-carbon bonds via carbocation chemistry, followed by β-scission and hydrogenation of unsaturated molecules, as shown in Fig. 3a [20]. The reactions are carried out at lower process temperature and result in reduced amounts of olefins, aromatics, and coke formation. Hydrocracking typically occurs in the presence of a bifunctional catalyst (consists of metallic and acidic sites supported on various materials) in a stirred batch autoclave at moderate temperature (300–450 °C) and a hydrogen pressure of 2–15 MPa [31].

Vlachos et al. selectively converted HDPE to liquid fuels such as diesel, jet and gasoline-range hydrocarbons via tandem catalysis in the presence of mechanically blended Pt/WO_3/ZrO_2 with HY (30) zeolite at 225 °C, resulting in a high yield of 85 % [33]. Similarly, Korley et al. investigated the deconstruction of HDPE in the presence of same catalyst system [21]. Moreover, the authors reported the effect of the additives (antioxidants- and slip agent-containing) present in the HDPE base resin over metal acid balance and on the yield of gas and liquid products

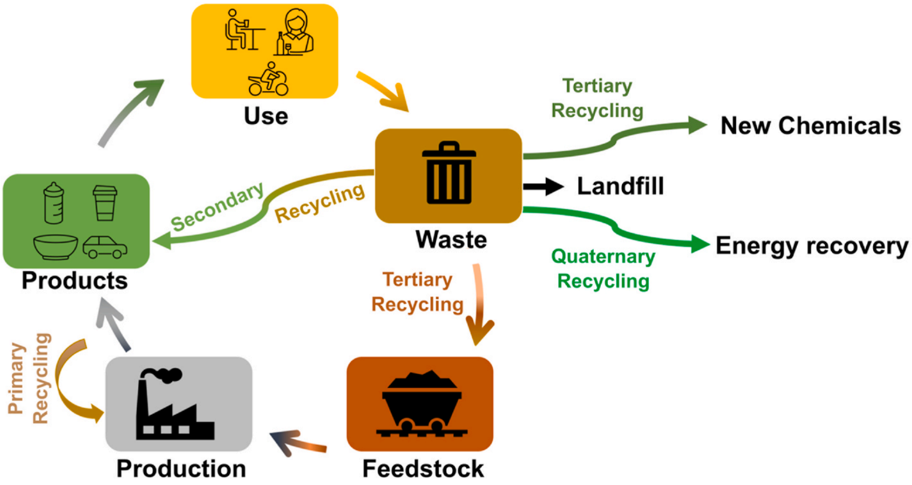


Fig. 1. Different approaches to the recycling of plastic, including primary, secondary, tertiary, and quaternary recycling.

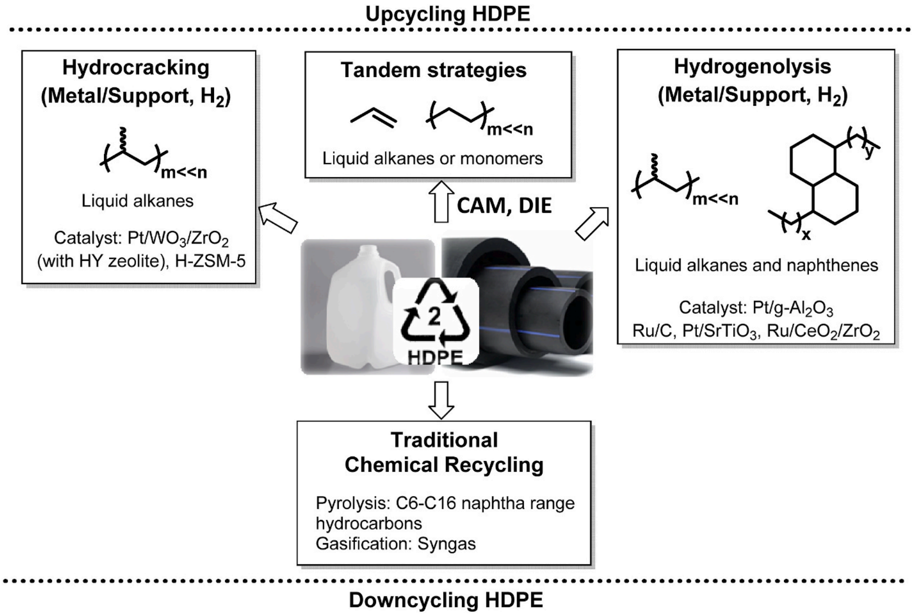


Fig. 2. Different chemical recycling (upcycling and downcycling) methods of HDPE and the resulting products.

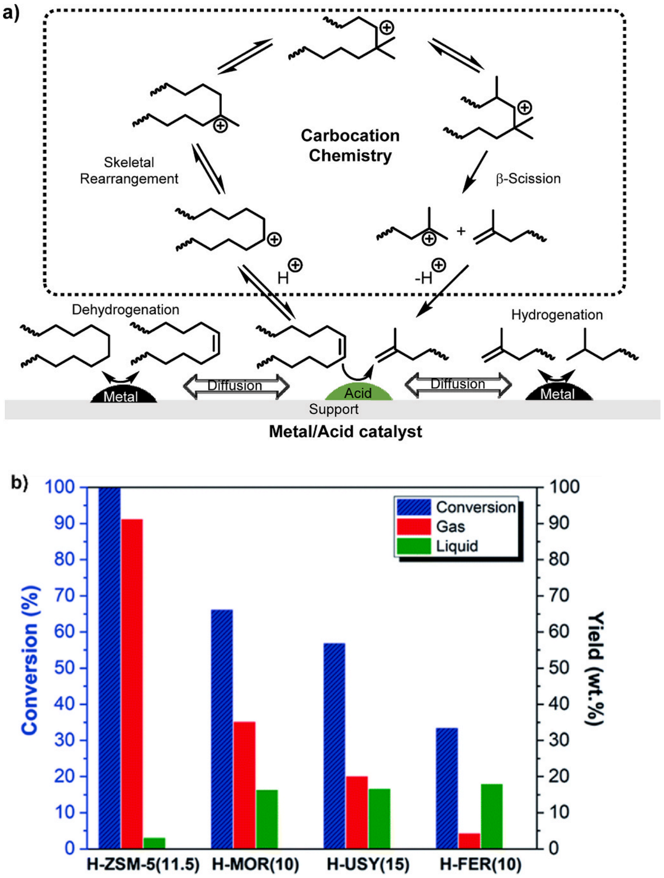


Fig. 3. **a)** General hydrocracking mechanism of polyethylene using metal/acid catalyst resulting in short-chain hydrocarbons. In this process the polymer is dehydrogenated, disintegrated via carbocation chemistry and finally hydrogenated to saturated hydrocarbons [20]; Copyright 2023. Reproduced with permission from Wiley-VCH GmbH. **b)** Conversion and yield of HDPE to gas and liquid with respect to different catalysts for 60 min at 300 °C, 20 bar H_2 [32]. Copyright 2022. Adopted with permission from Royal Society of Chemistry.

obtained.

In 2022, Costa and Ribeiro et al. conducted an experiment on hydrocracking of HDPE (M_w = 155 kg/mol) using four commercially available zeolites: H-USY, H-MOR (large pore), H-ZSM-5 (medium pore), and H-FER (small pore), with a similar Si/Al molar ratio (10–15) [32]. They found that H-ZSM-5 was the most effective catalyst for the 100 % conversion of HDPE, with a high likelihood of producing lighter alkanes in the C_3–C_5 range, as shown in Fig. 3b. Additionally, H-ZSM-5 enabled complete recovery of its initial activity upon regeneration. The study also highlighted the importance of acidity and porous structure in the hydrocracking process and ranked the activity of catalysts as follows: H-ZSM-5 ≥ H-MOR ≥ H-USY ≥ H-FER.

3.2.2. Hydrogenolysis

Hydrogenolysis is a process where a C–C single bond is cleaved by hydrogen in the presence of a monofunctional metal catalyst, such as Pt and Ru, supported on various materials. In this process, both polymers and hydrogen are absorbed by the metal-supported materials, facilitating the scission process of the polymers to the subsequent hydrocarbon fragments, as shown in Fig. 4a [34].

Delferro et al. used a Pt/STO catalyst to transform HDPE (laboratory and post-consumer) into value-added products by hydrogenolysis [36]. The catalyst was prepared using atomic layer deposition (ALD) with different numbers of cycles to obtain a series of Pt NP loading on $SrTiO_3$ (STO). They achieved a high-quality lubricant product with a yield of 47 % from PE (M_n = 8150 Da, M_w = 22,150 Da, and dispersity ($Đ$ = 2.7)) and investigated different loading of Pt (1.7 %–18.8 %). The results revealed completely gaseous hydrocarbons (C_1–C_8) and high-quality liquid for low loading and higher loading of Pt, respectively. They also compared these catalysts with the commercial Pt/g-Al_2O_3. With the same catalyst Pt/STO synthesized in scalable amount via strong electrostatic adsorption, Poeppelmeier et al. hydrogenated HDPE to wax products with a conversion of 99 % with a loading of 3.6 wt% Pt under similar conditions [37]. In 2020, Scott et al. reported the conversion of HDPE (M_w = 53,500 Da) to low molecular weight liquid/wax products in the presence of catalyst Pt/g-Al_2O_3 with 1.5 % Pt loading at 280 °C, as shown in Fig. 4b. The tandem synthesis was performed in the absence of solvent or hydrogen gas to obtain products, which constitute of long chain alkylaromatics and alkylnaphthenes in yields up to 80 % [35].

In 2021, Lin et al. depolymerized HDPE into jet-fuel- and lubricant-range hydrocarbons in the presence of Ru/C catalyst in *n*-hexane solvent

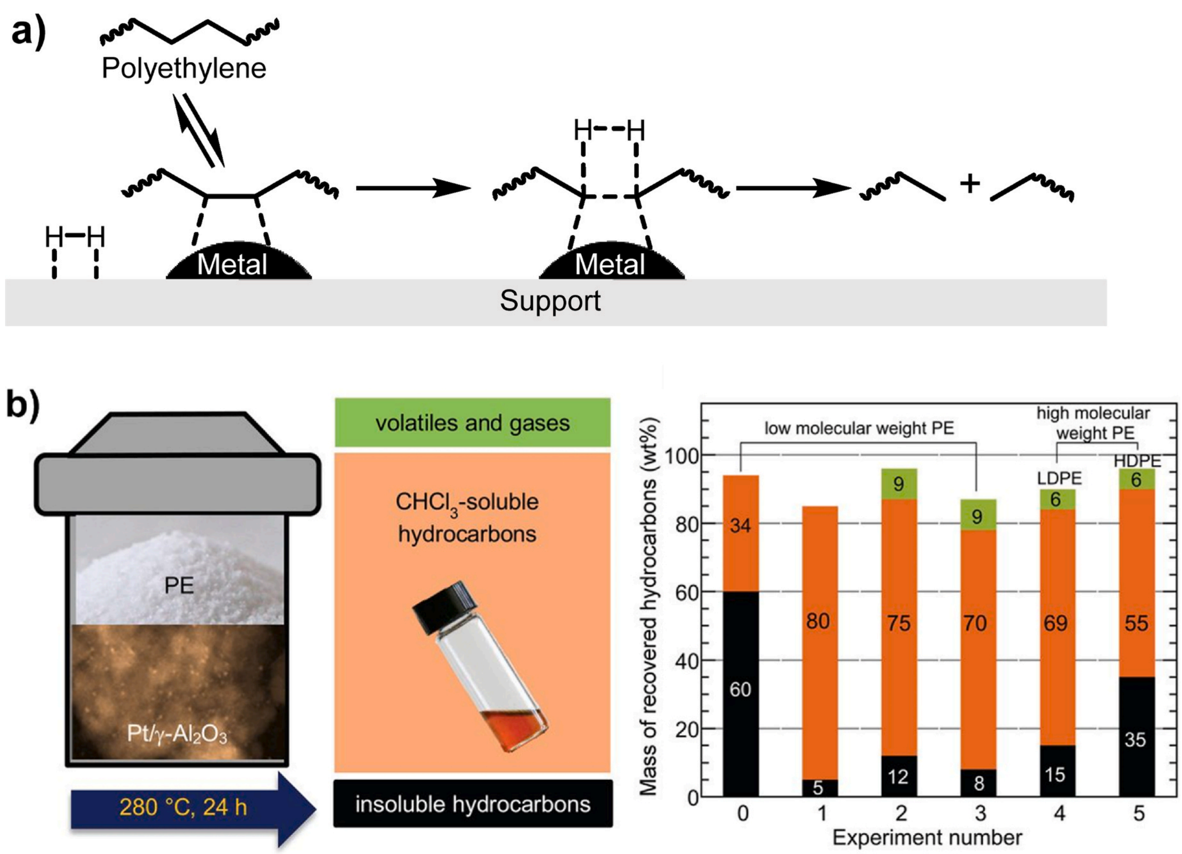


Fig. 4. **a)** Cracking pathway of polyethylene using hydrogenolysis in the presence of metal catalyst [34]; **b)** Hydrogenolysis of PE, product fractions and distribution of hydrocarbons at 280 °C after 24 h in the presence of Pt/γ-Al$_2$O$_3$ [35]. Copyright 2020. Adopted with permission from the American Association for the Advancement of Science.

under mild condition at 220 °C [38]. Moreover, the product distribution was tuned by regulating hydrogen pressure, active-metal particle size, and solvents. The maximum optimized yield of the fuel obtained was 90 % in minimum time of 1 h under 60 bar H$_2$. Tamura and Tomishige et al. studied a novel heterogenous reusable catalyst based on CeO$_2$ supported Ruthenium (Ru/CeO$_2$), which resulted in the conversion of HDPE and other polyolefins to valuable chemicals such as liquid fuels and waxes in high yields (83–90 %) at lower temperature (200 °C) compared to the above mentioned reports [39]. In 2022, the same group reported Zirconia supported Ru with high-temperature-calcined ZrO$_2$ (800 °C) revealing a higher activity compared to previously reported Ru/CeO$_2$ and other metal based catalyst such as Pt and Ni [40].

3.3. *Tandem reaction strategies involving olefin intermediates*

A tandem reaction, also called a cascade or domino reaction, is a chemical process involving at least two consecutive reactions. Each subsequent reaction only occurs because of the chemical functionality formed in the previous step. Tandem catalytic cross alkane metathesis (CAM) to produce aliphatic hydrocarbon from *n*-alkanes was initially developed by Goldmann and Brookhart et al. [41,42] Later, they applied this method for PE to convert into waxes and low molecular weight oils [43].

A three-step strategy for breaking down HDPE into low molecular weight alkanes and waxes was developed by Guan and Huang et al. [44] The process involves dehydrogenation of PE to introduce internal olefinic functionality, using an Ir-based catalyst, cross-metathesis with alkene using Re$_2$O$_7$/g-Al$_2$O$_3$ as a catalyst, and hydrogenation to form saturated low molecular weight alkanes using an Ir-based catalyst, as shown in Fig. 5. Three types of dehydrogenation Ir-based catalysts with different ligands ($^{t-\text{Bu}}$PCP, $^{t-\text{Bu}}$POCOP, $^{i-\text{Pr}}$POCOP) in the presence of

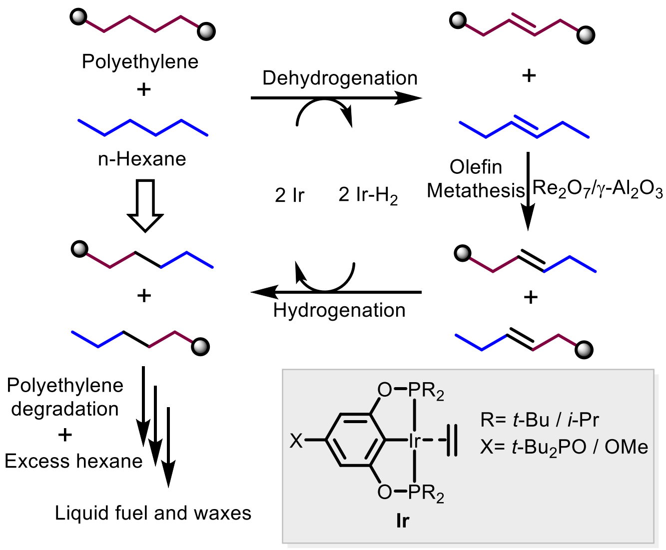


Fig. 5. Disintegration of polyethylene into lighter alkanes via cross-alkane metathesis (CAM). Dehydrogenation in the presence of Ir-based pincer (Ir), followed by cross metathesis using Re based catalyst and subsequently hydrogenation resulting in shorter hydrocarbon chains. Repeated cycles lead to PE degradation to liquid fuel and waxes [44]. Copyright 2016. Reproduced with permission from the American Association for the Advancement of Science.

the cross-metathesis catalyst were investigated. Among which POCOP ligand-based catalyst resulted in a better yield (98 %) with laboratory-grade HDPE (M_w = 3350 Da) compared to PCP ligand-based counterparts with low yields. It was believed the higher regioselectivity for the formation of internal alkenes with POCOP ligand-based catalysts compared to PCP ligand-based catalysts. This study also revealed promising results with both commercial PE plastic, post-consumer polyethylene, and ultrahigh molecular weight PE, thus, providing a better solution for feedstock recovery from PE plastic waste.

In 2022, a few groups reported the use of tandem catalysis for the disintegration of HDPE using similar techniques via dehydrogenation and subsequent isomerization ethanolysis (DIE) to obtain propylene as the product. Hartwig et al. developed dehydrogenation of polyethylene in the presence of Ir^{tBu}POCOP catalyst (**Ir1**) and *tert*-butyl ethylene (TBE, H_2 acceptor), which was further disintegrated to propylene with yields surpassing 80 % under ethylene pressure in the presence of varying combinations of a second-generation Hoveyda-Grubbs metathesis catalyst (**Ru1**) and $[PdP(tBu)_3(m\text{-}Br)]_2$ (**I**) as isomerization catalysts (Fig. 6) [45]. The DIE test was also performed on post-consumer polyethylene (PE) material, resulting in a yield of 57 %. Scott and Guironnet et al. used a similar DIE technique on vinyl-terminated polyethylene in the presence of a ruthenium-based ethenolysis catalyst, Ultracat (**Ru2**), and homogenous or heterogenous catalysts [46]. In the presence of **Ru2** and homogenous isomerization catalyst **I,** a high selectivity of propylene (94 mol% in 1 h) was obtained, as shown in Fig. 6b. However, the high price and lower thermal stability of the catalyst led to the investigation of a heterogenous isomerization catalyst. MTO/Cl–Al_2O_3 (**Re**), which is methyltrioxorhenium (MTO) supported on and activated by chlorinated alumina (Cl–Al_2O_3), was employed as a heterogenous isomerization catalyst to obtain 50 % light olefins. The propylene selectivity was 95 %, and the catalyst was completely deactivated within 7 h. Transfer dehydrogenation of saturated PE using a heterogenous catalyst (Pt/g-Al_2O_3) and consecutive ethenolysis/isomerization resulted in a low yield of propylene due to the small extent of unsaturation of PE. Performing all three catalytic reactions in tandem using dehydrogenation catalyst Ir-based pincer (**Ir2**), and **Re** with monounsaturated PE resulted in a low yield of propylene (30 wt%).

LaPointe, Delferro and Coates et al. used **Ir1** catalyst to introduce olefinic functionalities to HDPE with a concentration of 0.79 mol% of internal olefin without the use of an alkene acceptor [28]. Further, cross metathesis with 2-hydroxyethyl acrylate, followed by hydrogenation can obtain telechelic PE macromonomer from unsaturated HDPE. The telechelic macromonomers, containing 0.69 mol% internal olefin, were processed using the above-mentioned procedure to obtain Oligo1, as illustrated in Fig. 7a. Later, polyester Poly1 (RP1) was synthesized through a polycondensation reaction by polymerizing Oligo1 in the presence of $Ti(O^nBu)_4$, which allowed the incorporation of cleavable functionalities. However, the M_w of Poly1 is low (33 kDa) compared to the M_w of waste polyethylene (120 kDa), therefore affecting the tensile

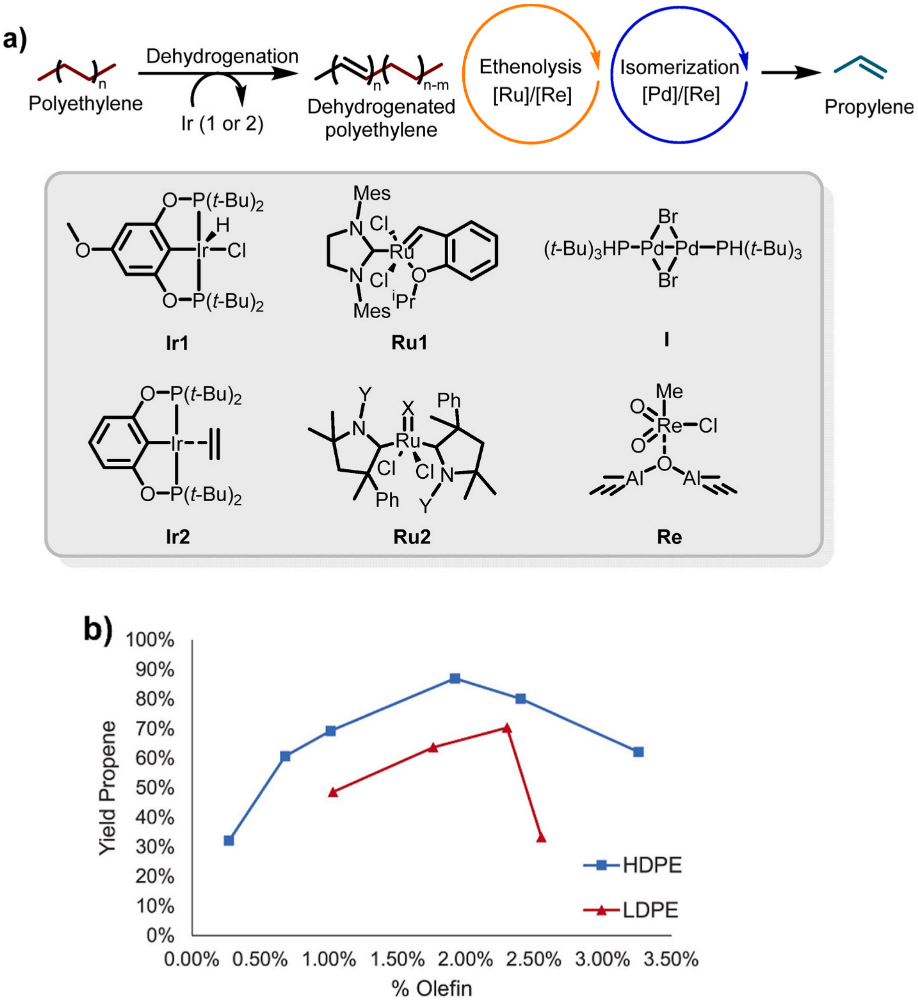


Fig. 6. **a)** Tandem reaction process for the conversion of HDPE to a valuable raw material, propylene, using dehydrogenation and isomerizing ethenolysis (DIE) [46]. Iridium-based pincer (**Ir1**, **Ir2**) as a catalyst for the dehydrogenation process introducing unsaturation in the PE backbone, homogenous **Ru1** or **Ru2** or heterogenous **Re** as cross-metathesis catalyst with ethylene, and **I** or **Re** for isomerization of double bond resulting in the formation of propylene [45,46]; **b)** Dehydrogenation and subsequent isomerization ethanolysis of HDPE resulting in propane surpassing a yield of 80 % with 1.96 % dehydrogenation [45]. Copyright 2022. Adopted with permission from the American Association for the Advancement of Science.

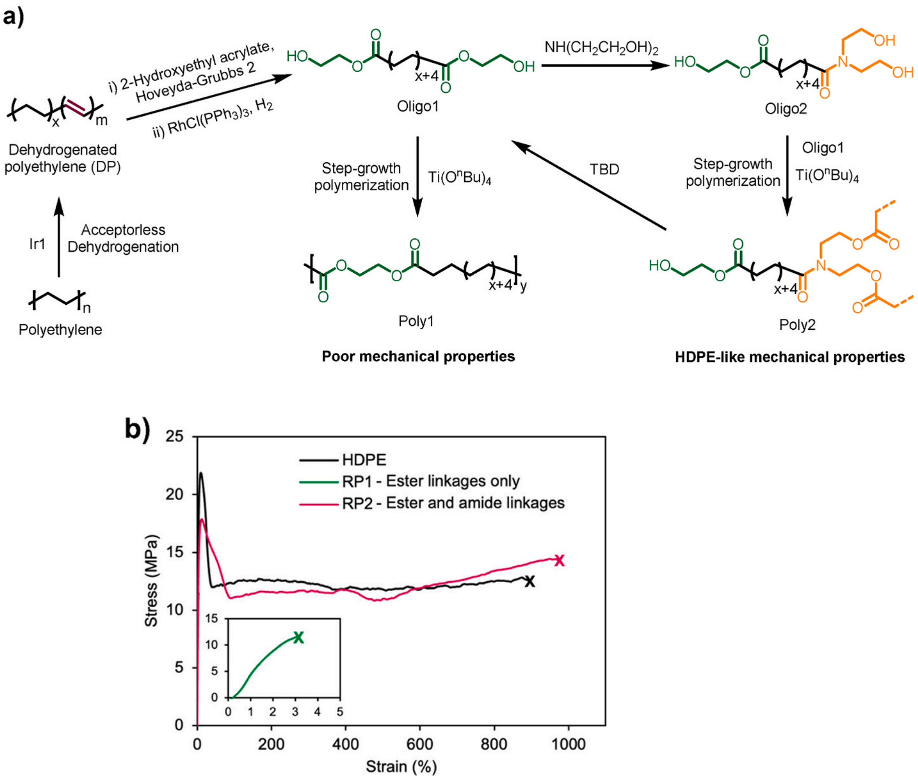


Fig. 7. a) A three-step process to synthesize chemically recyclable polyester exhibiting HDPE-like mechanical properties from post-consumer polyethylene; **b)** Tensile properties of post-consumer waste HDPE, Poly1 (RP1) and Poly2 (RP2) [28]. Copyright 2022. Adopted with permission from American Chemical Society.

properties of the polymer. In order to enhance the mechanical properties, Oligo2 was synthesized with amide functionalities using a trifunctional cross-linker diethanol amine (10 equiv) in comparison to Oligo1. The mixture of Oligo1 and Oligo2 had 8 mol% of amide functionalities compared to all functionalities in Oligo1 + Oligo2. Further, Poly2 was obtained by subjecting Oligo1 and Oligo2 to polycondensation. The material produced had a yield strength of 18 MPa and a strain at break of 970 %, which was comparable to the original post-consumer waste HDPE, as shown in Fig. 7b. Additionally, the process of depolymerizing Poly2 (RP2) into depolymerized Oligo1 was examined and successfully accomplished with the help of a catalytic amount of triazabicyclodecene (TBD) and an excess of ethylene glycol. The conversion reached over 95 %.

4. “HDPE-like” materials

In addition to conventional recycling and upcycling HDPE waste, a promising alternative strategy is to design and synthesize new polymers by introducing potentially degradable functionable groups, such as ester [47,48], acetal [49], amide [50,51], thioester [52] etc., into the HDPE backbone while keeping its properties. These in-chain degradable functional groups as break points in the HDPE chains can be recycled chemically by solvolysis, resulting in short fragments, which can be further polymerized to afford materials with similar properties to their original polymers and achieve closed-loop recycling of “high-density polyethylene-like” or “high-density polyethylene mimic” materials (Fig. 8). To date, many research groups have attempted to synthesize

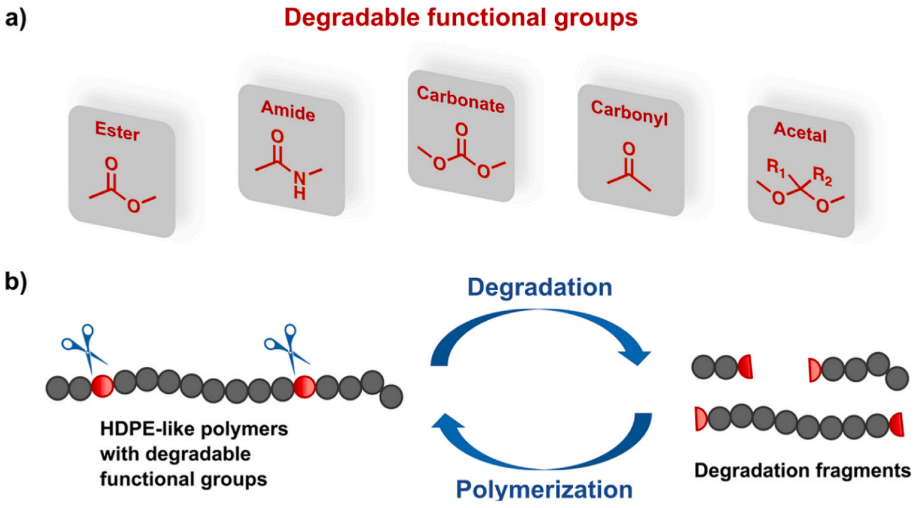


Fig. 8. a) Degradable functional groups within “HDPE-like” polymer backbone; **b)** A closed-loop recycling of “HDPE-like” materials.

linear aliphatic polymers containing these degradable functional groups. However, many properties of these polymers exhibit limitations, preventing a complete resemblance of the characteristics of commodity HDPE. For instance. Zhang et al. reported that sulphur-containing “HDPE-like” plastic had two diffraction peaks at 21° and 24°, with stress values ranging from 15.1 MPa to 28.9 MPa, and the elongation at break ranging from 480 % to 702 %, which were comparable to commercial HDPE [53]. However, the melting temperature (T_m) of these polymers was between 55 °C and 75 °C, which is substantially lower than that of commercial HDPE. Spoljaric et al. reported a series of polyamides with good impact resistance and excellent stiffness-to-toughness balance comparable to HDPE, but the T_m of short-chain polyamides were above 200 °C, substantially higher than that of HDPE [50]. Some relevant earlier reviews have given summaries of the preparation, thermal-mechanical properties, and degradability of HDPE alternative materials [10,13,54,55]. Owing to the advances in chemical synthesis, polymerization conditions, and analytical techniques, an increasing number of studies have emerged, yielding a great number of sustainable and “HDPE-like” materials. Concerning the scope of this review, “HDPE-like” or “HDPE mimic” materials are considered to polymers that have 10 or more linear aliphatic methylene groups between functional groups with a melting temperature range of 100 °C–150 °C [54,56]. Polymers that cannot meet these criteria are excluded from consideration.

A lot of efforts have been made in recent years to develop sustainable “HDPE-like” polymers [10,54,72]. Notably, techniques such as polycondensation of long-chain aliphatic monomers [57,73], ring-opening polymerization (ROP) [74], ring-opening metathesis (co)polymerization (ROMP) [75], and acyclic diene metathesis (ADMET) polymerization [76–78], have been explored to create more friendly alternatives to traditional HDPE. Specifically, polycondensation involves the condensation of long-chain α, ω-difunctional monomers such as diols, diesters, diamines and hydroxyl esters with release of small molecules, leading to the incorporation of degradable functional groups, including esters and amides within the methylene segments of the backbone (Fig. 9a). ROP is a reaction in which one polymer chain has a reactive center on its terminal end, reacting with another cyclic monomer bearing degradable ester groups, thereby opening the ring system to form a long-chain aliphatic polyester (Fig. 9b). ROMP represents a type of olefin metathesis chain-growth polymerization using strained cyclic olefins to produce polymers and copolymers containing degradable functional groups (Fig. 9c). ADMET is a step-growth polycondensation reaction of α, ω-dienes bearing degradable functional groups along methylene units with the release of ethylene as the byproduct. ADMET is consistently followed by hydrogenation to yield polymers with comparable properties to HDPE (Fig. 9d). This section is composed of various methodologies and instances for the synthesis of “HDPE-like” materials, including polycondensation, ROP, ROMP, ADMET and other polymerization approaches [57,59,60,62,65,66,70]. Table 1 summaries some recent efforts.

4.1. Polycondensation of long-chain aliphatic monomers

The traditional polycondensation routes to synthesize these degradable long-chain aliphatic polycondensates are divided into two categories: (1) synthesized from an AB-type monomer X_1-$(CH_2)_m$-X_2; (2) synthesized from two AA and BB-type long-chain α, ω-difunctional monomers X_1-$(CH_2)_n$-X_1 [54]. One advantage is that these long chain

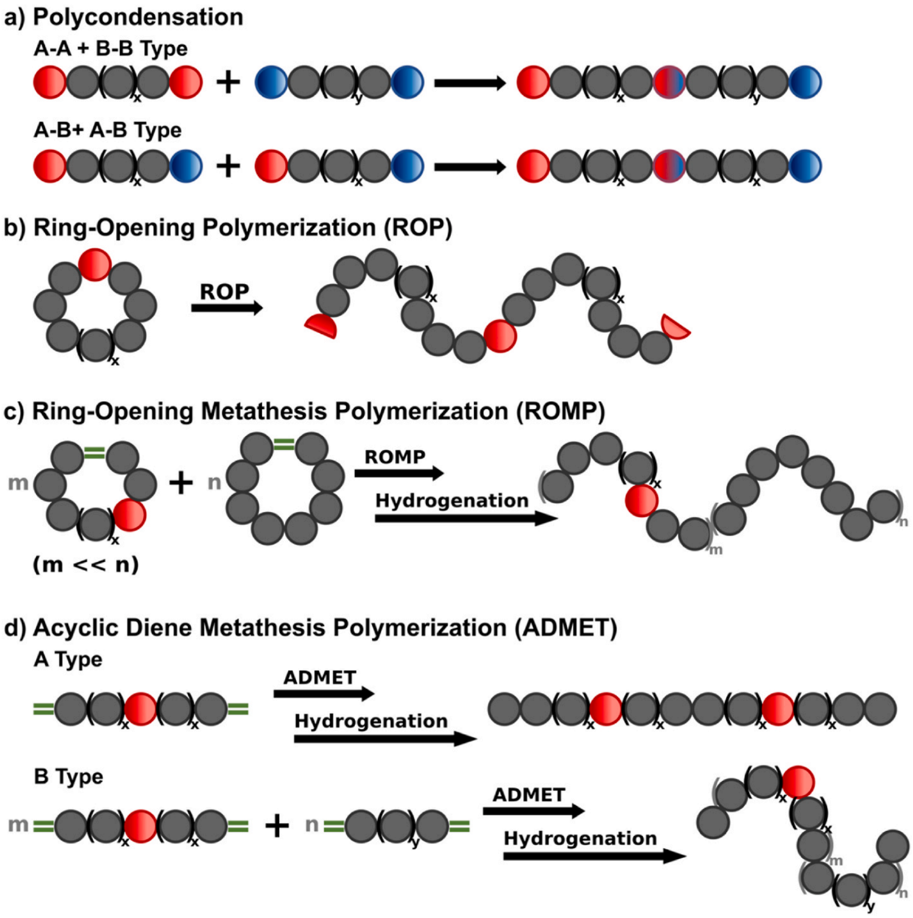


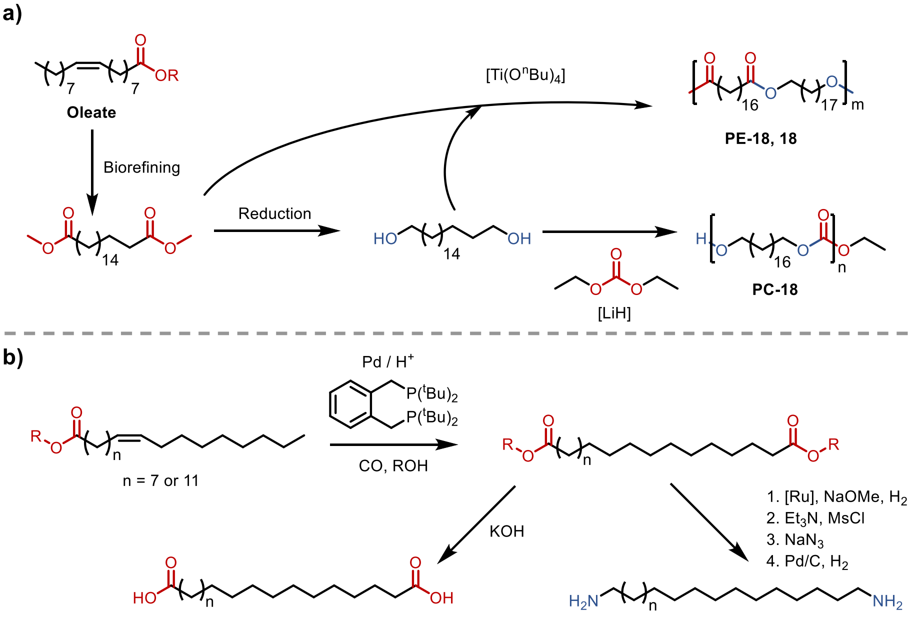
Fig. 9. Polymerization methods of “HDPE-like” materials. **a)** polycondensation; **b)** ring-opening polymerization; **c)** ring-opening metathesis polymerization; **d)** acyclic diene metathesis polymerization.

Table 1
Thermal and mechanical property summary of "HDPE-like" materials synthesized via different polymerization methods.

Polymerization methods	Degradable functional group	M_n (kg/mol)	T_m (°C)	σ (MPa)	ε (%)	*E* (MPa)	Ref.
Polycondensation	Ester	50	98.7	22	470	910	[57]
	Carbonate	90	87.3	16	350	640	[57]
	Amide	10	156, 152				[58]
ROP	Ester	10–60	98–106				[59]
ROMP	Ester	31.2–50	105–131.7				[60]
	Orthoester	0.9–12.7	86–117				[61]
ADMET	Ester	8.9–15.5	100–133				[62]
		10	108				[63]
	Acetal	10.3–13	104–131				[64]
	Carbonate	10.6–13.5	102–132				[64]
Other	Amide	55, 48	125, 121	23, 22	645, 600	430, 300	[65]
			123–133	13–17	520–1037	570–750	[66]
	Ester		124–130	15–17	490–880	590–730	[66]
			120–123	11–37	40–380	300–820	[67]
		26.5–41.6	127.4–133.9				[68]
	Ketone	1070	147				[69]
		220	134	26.7	470	1062	[70]
		58	130				[71]

monomers can be obtained from plant oils, which are one of the most abundant renewable resources [79–81]. However, polycondensation reactions have several drawbacks, including the difficult control of molecular weights and dispersity. In addition, the conditions of high temperature and vacuum could make this approach energy intensive, and high temperature can also trigger thermal decomposition reactions. Side-reactions and evaporation of monomers can result in a stoichiometric imbalance of reactants, which makes the synthesis of high molecular weight polymers difficult [82]. Since the high molecular weight is very necessary for high performance polymer materials, a lot of studies have been focused on improving the molecular weights of long-chain aliphatic polycondensates.

Mecking et al. reported a significant advancement in the realm of sustainable polymer materials by demonstrating the closed-looped chemical recycling of "HDPE-like" materials (Scheme 1a) [57]. Polyester-18, 18 (PE-18, 18) was synthesized by $Ti(O^nBu)_4$ catalyzed polycondensation with stoichiometric amounts of C_{18} diester and diol, yielding a weight average molecular weight (M_w) of approximately 80 kg/mol. Additionally, polycarbonate-18 (PC-18) with M_w of approximately 300 kg/mol was also synthesized by reacting the C_{18} diol with diethyl carbonate. The starting materials C_{18} diester and diol were obtained from commercially available 1,18-octadecanedioic acid, derived from scalable biorefining of plant oils through olefin metathesis [83]. Upon degradation, PE-18, 18 could be depolymerized in MeOH with or without a catalyst at 150 °C, yielding a near quantitative ratio of the C_{18} diester and C_{18} diol mixture. In the case of PC-18, depolymerization in basic EtOH yields the C_{18} diol and diethyl carbonate with a recovery rate of more than 96 %. Finally, the recycled monomers were successfully repolymerized, resulting in high molecular weights PE-18, 18 and PC-18 again. They also investigated the thermal-mechanical properties of PE-18, 18 and PC-18 and found that the melting temperature, Young's modulus and elongation at break were 910 MPa and 470 % for PE-18, 18, and 640 MPa and 350 % for PC-18, respectively (Fig. 10b and c). They were comparable to those of commercial HDPE [84]. The WAXS diffraction patterns of the prepared materials corresponding to the orthorhombic unit [110] and [200] were closed resembled to HDPE, indicating that the incorporation of ester and carbonate linkages did not significantly influence the crystalline PE structure (Fig. 10a). Importantly, the performance of the recovered polymers was comparable to those of the original PE-18, 18 and PC-18, confirming the successful



Scheme 1. **a)** Synthesis of degradable HDPE-like polymers with plant oil or microalgae oil-derived monomer feedstock [57]; Copyright 2021. Reproduced with permission from Springer Nature. **b)** synthesis of diacids and diamines from methyl oleate and erucate [58].

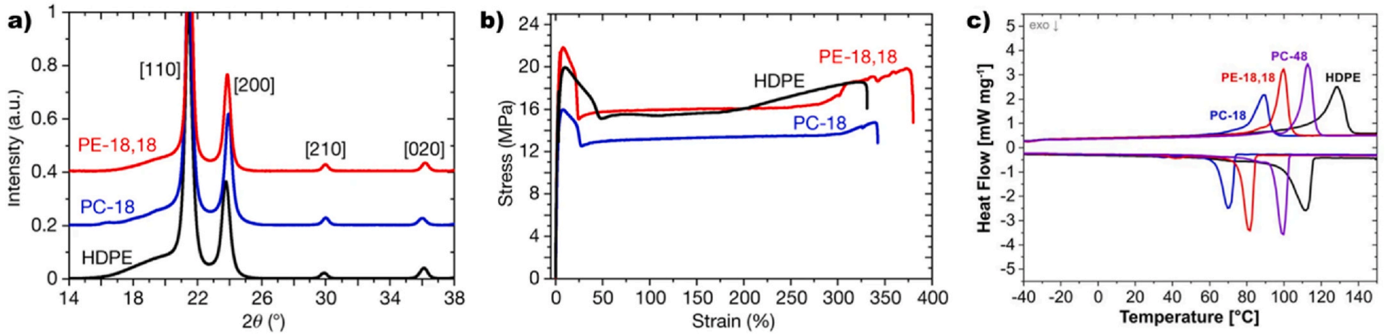


Fig. 10. **a)** WAXS of PE-18, 18, PC-18 and commercial HDPE; **b)** stress-strain curves of PE-18, 18, PC-18 and commercial HDPE; **c)** DSC traces of PE-18, 18, PC-18 and commercial HDPE [57]. Copyright 2021. Adopted with permission from Springer Nature.

synthesis of closed-loop chemically recyclable "HDPE-like" polymers.

Long-chain aliphatic polycondensates, like polyesters and polycarbonates, differ from their shorter chain aliphatic polycondensates, where the polar groups on the polymer main chain largely determine their physical properties. Due to a great number of methylene units in the backbone, these long-chain aliphatic polycondensates not only have similar mechanical properties as HDPE, but also show unique degradability, compostability, and biocompatibility [85,86]. Consequently, these polymers are frequently discussed as "HDPE mimics" or "HDPE-like" (Fig. 11).

Long-chain aliphatic polyamides have also been reported as "HDPE mimics", which could be synthesized by polycondensation of diamines and dicarboxylic acids. These starting materials are easily obtained from vegetable oils. Meier et al. presented an efficient method to prepare various long-chain aliphatic polyamides from vegetable oils [87]. Mecking et al. reported long-chain aliphatic polyamides PA-23, 19 and PA-23, 23 with molecular weight around 10 kg/mol, exhibiting a melting temperature 156 °C and 152 °C, respectively (Scheme 1b) [58].

4.2. Ring-opening (metathesis) polymerization

Ring-opening polymerization (ROP) has already been used to synthesize a variety of long-chain aliphatic polyesters. Unlike polycondensation, which requires removal of small molecules, high temperature, and bulk condition to obtain high molecular weights. ROP could be performed in solution, resulting in a lower viscosity, and a linear relationship of molecular weight and monomer conversion. Therefore, long-chain aliphatic polyesters with high molecular weights could be obtained via ROP under mild conditions.

Ring-opening polymerization (ROP) of macrolactones has been proved as an efficient method to synthesize high molecular weight long-chain aliphatic polyesters. Mecking and Williams et al. reported ROP of ω-pentadecalactone (C_{15}), nonadecalactone (C_{19}) and tricosalactone (C_{23}) using an yttrium phosphasalen catalyst with molecular weights ranging from 10 kg/mol to 60 kg/mol and melting temperatures ranging from 98 °C to 106 °C (Scheme 2a) [59].

Unlike polycondensation and ROP, where the amount of methylene units between every adjacent pair of functional groups is the same, long-chain aliphatic polymers with a random distribution of functional groups can be obtained using the copolymerization of degradable functional groups containing olefinic monomers with hydrocarbon olefinic monomers by ring-opening metathesis polymerization (ROMP). ROMP could afford relatively high molecular weight polymers without an extremely high conversion of monomers.

Duchateau et al. has reported the influence of methylene-to-ester ratios and random distribution of ester groups on the physical properties of long-chain aliphatic polyesters (Scheme 2b) [60]. They conducted ROMP of ambrettolide and *cis*-cyclooctene followed by hydrogenation, yielding long-chain aliphatic polyesters with M_n ranging from 31.2 kg/mol to 50 kg/mol. They found that as methylene-to-ester ratio increased from 23 to 229, the T_m of these long-chain aliphatic polyesters increased from 105.0 °C to 131.7 °C (Fig. 12a). When the methylene-to-ester ratio was high enough, the random distribution of ester groups had no effect on the T_m and crystallinity of long-chain aliphatic polyesters, which was comparable to HDPE.

Wurm et al. synthesized degradable polyethylene mimics containing orthoester groups via ROMP of 1,5-cyclooctadiene with a diverse of cyclic orthoester monomers, yielding linear copolymers with molecular

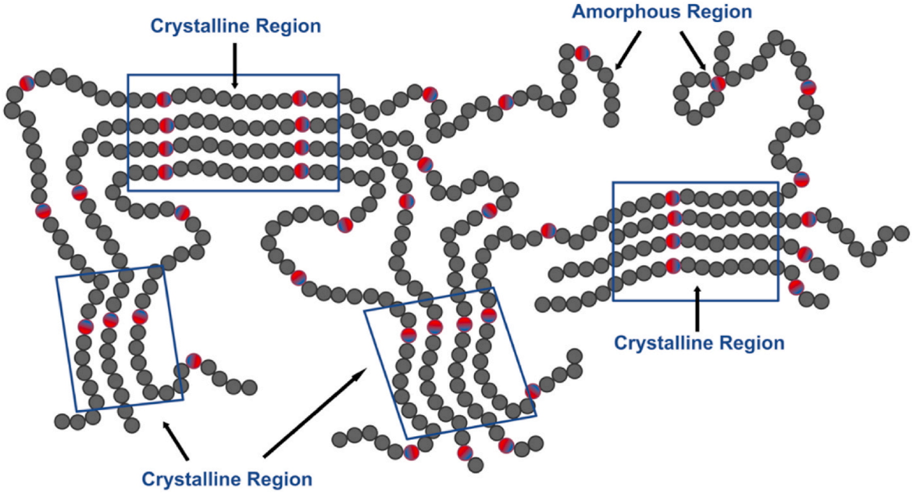
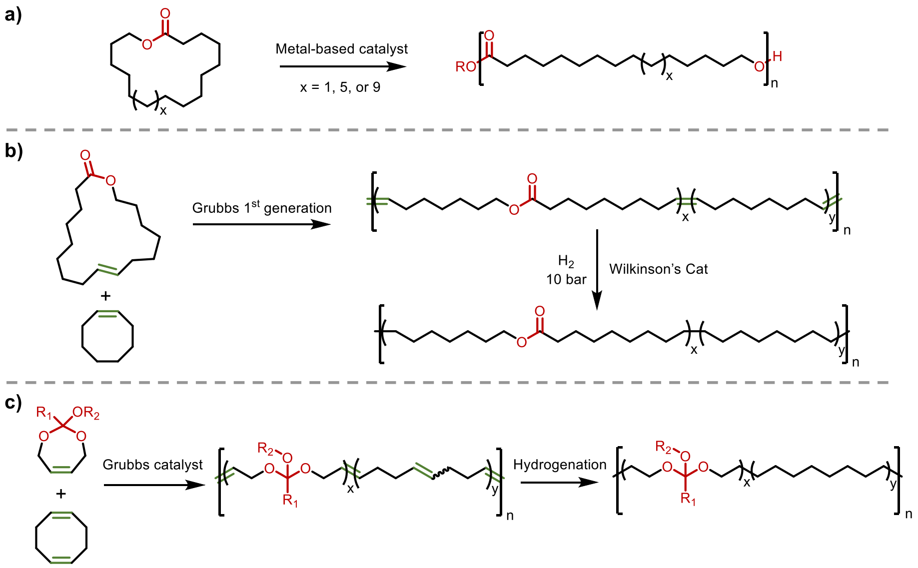


Fig. 11. A proposed model to illustrate crystalline and amorphous regions of "HDPE-like" materials.



Scheme 2. **a)** Ring-opening polymerizations of macrolactones ω-pentadecalactone (C_{15}), nonadecalactone (C_{19}) and tricosalactone (C_{23}) by metal-based catalyst [59]; **b)** Ring-opening metathesis (co)polymerization of ambrettolide with *cis*-cyclooctene and subsequent hydrogenation [60]; **c)** Ring-opening metathesis (co) polymerization of orthoester with 1,5-cyclooctadiene and subsequent hydrogenation [61].

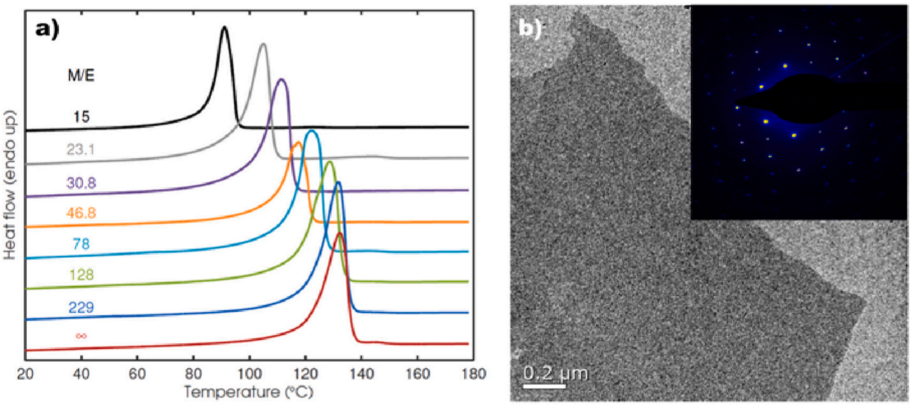


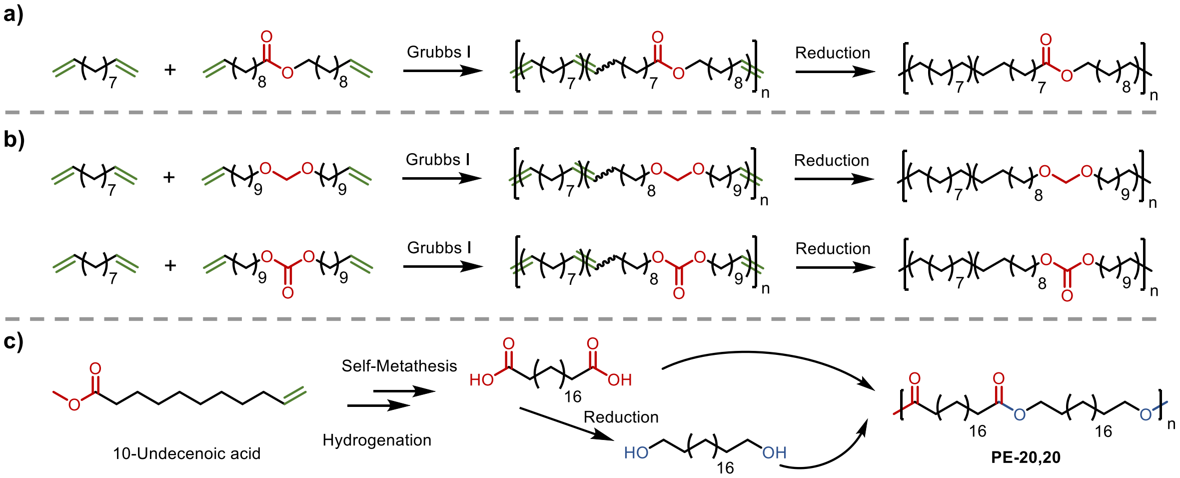
Fig. 12. **a)** DSC traces of long-chain aliphatic polyesters [60]; Copyright 2013. Adopted with permission from American Chemical Society. **b)** TEM bright-field micrograph and corresponding diffraction pattern of long-chain polyorthoesters [61]. Copyright 2019. Reprinted with permission from American Chemical Society.

weight up to 38 kg/mol. Subsequent hydrogenation of such copolymers produced semicrystalline "HDPE-like" materials (Scheme 2c) [61]. Notably, while mechanical property assessment of these materials proved challenging because of the brittle nature resulting from relatively low molecular weights, the T_m exhibited an increase from 86 °C to 117 °C with increasing the number of methylene groups between the orthoester groups, making the material became more similar to HDPE. Additionally, electron diffraction showed the single crystal pattern of flat-on orthorhombic PE crystals (Fig. 12b). The incorporation of orthoester groups would not change the crystal structure of these polymers, maintaining a crystal structure similar to that of commercial HDPE. Their study represented a potential advantage of biodegradable HDPE mimics based on orthoester linkages compared to commercial HDPE.

4.3. *Acyclic diene metathesis polymerization*

Acyclic diene metathesis polymerization (ADMET) of linear α,ω-diene monomers could afford regular polyolefins, followed by hydrogenation to produce "HDPE-like" materials with functionality separated by a constant number of methylene spacers. In the past years, researchers tried to incorporate a higher number of methylene units between functional groups and achieve "HDPE-like" properties. For example, Mecking et al. synthesized long-chain aliphatic polyesters by ADMET copolymerization of undec-10-en-1-yl undec-10-enoate and undeca-1,10-diene followed by hydrogenation. These ester groups decreasing from 52.6 to 0.9 per 1000 methylene units randomly distributed in the polyethylene backbone, resulting in an increase of T_m from 100 °C to 133 °C (Scheme 3a) [62]. They demonstrated that a lower content of ester groups was necessary to achieve thermal properties of polyethylene. Similarly, this conclusion also applies to long-chain aliphatic polyacetals and polycarbonates (Scheme 3b). They found that melting temperature of polyacetals increased from 104 °C to 131 °C as acetal groups decreased from 21 to 1.5 per 1000 methylene units and melting temperature of polycarbonates increased from 102 °C to 132 °C as carbonate groups decreased from 30.6 to 1.1 per 1000 methylene units. In the comparison of the influence of ester, carbonate, and acetal groups on the thermal properties of long-chain polymers, carbonate groups have a more pronounced impact on T_m than ester groups because of its lower polarity and a less propensity for ordered layer formation. Polyacetals could form more complex and less uniform structures, resulting in "HDPE-like" polymers only at exceedingly low contents of acetal groups [64].

The remaining internal double bonds within the polymer backbone



Scheme 3. **a)** The synthesis of long-chain aliphatic polyesters by ADMET copolymerization and hydrogenation [62]; **b)** The synthesis of long-chain aliphatic polyacetals and polycarbonates by ADMET copolymerization and hydrogenation [64]; **c)** The synthesis of long-chain aliphatic polyesters by polycondensation of monomers obtained from 10-undecenoic acid [63].

during reduction could limit the crystallization and prevent the polymers from exhibiting fully "HDPE-like" thermal-mechanical properties. To overcome this limitation, researchers have proposed a strategy that amalgamates the metathesis reaction with polycondensation, thereby elevating molecular weight of polymers with similar thermol-mechanical properties to HDPE. Mecking et al. synthesized an unsaturated α,ω-dicarboxylic acid by a metathesis reaction to couple two undecanoic acid segments together, subsequently employing a hydrogenation reaction to yield a saturated long chain C20 diacid. Further reduction of the saturated long chain C20 diacid gave the corresponding C20 diol. Polycondensation of these two monomers yielded a polyester-20, 20 with a M_n of 10 kg/mol and a T_m of 108 °C similar to that of the hydrogenated polymer resulting from ADMET polymerization of undecenyl undecenoate (Scheme 3c) [63]. Similarly, the same methodology was employed to synthesize polyester-38, 23 and polyester-44, 23 with T_m of 109 °C and 111 °C, respectively. After polycondensation, all these long-chain aliphatic polyesters exhibited more "HDPE-like" properties than their ADMET polymerization-derived counterparts [56].

4.4. Other polymerizations

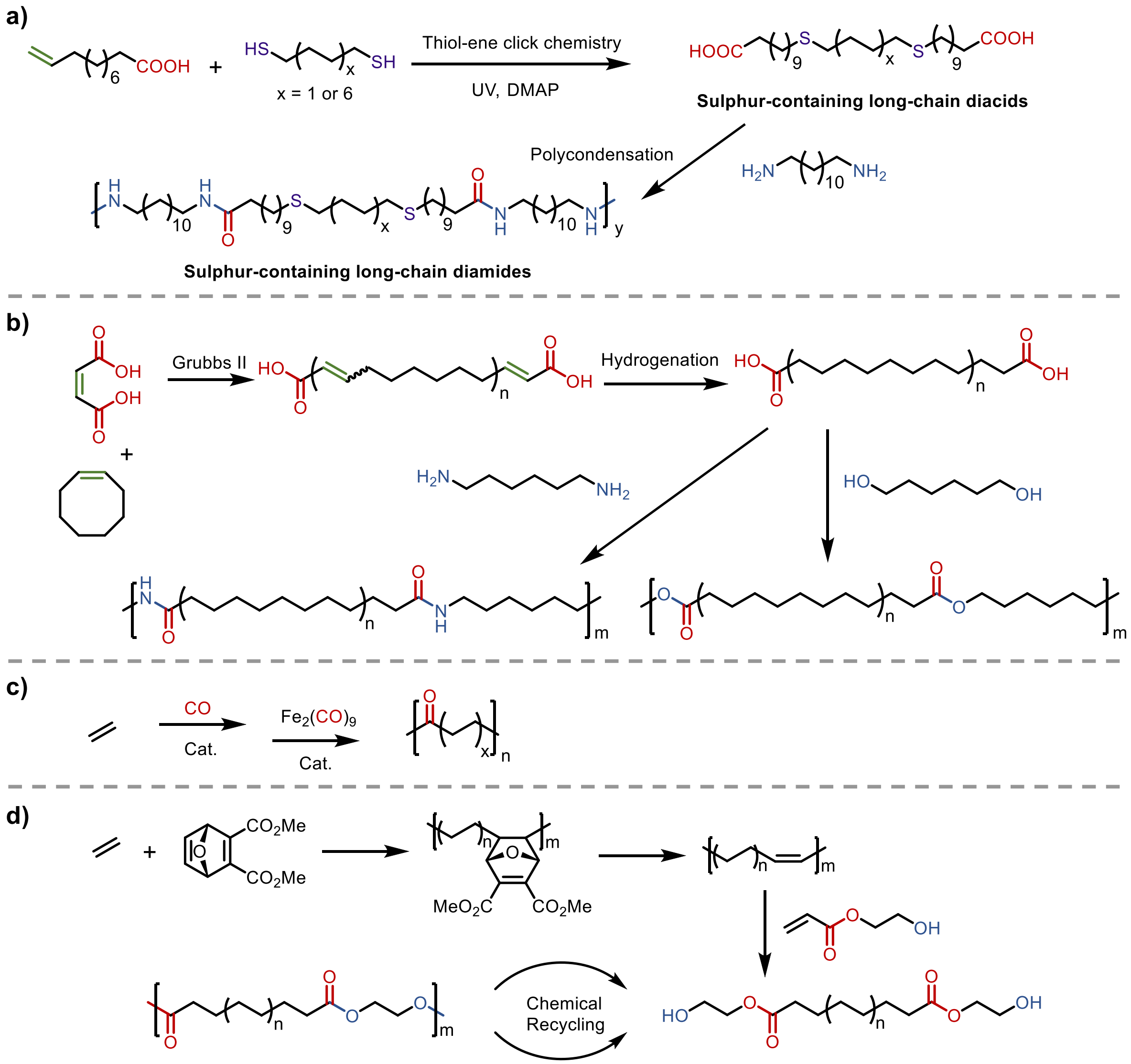
Seppälä et al. reported a series of sulphur-containing polyamides synthesized by polycondensation (Scheme 4a) [65]. In their approach, sulphur was initially introduced into the polyamide backbone through a thiol-ene click reaction of dithiol and 10-undecenoic acid monomers, resulting in an increase of aliphatic segment length. The subsequent polycondensation of these elongated sulphur-modified linear polyamides with dodecamethlenediamine yielded polymers with a M_n approaching 55 kg/mol. Consequently, the resulting polyamides exhibited T_m of 125 °C and 121 °C, tensile strength, Young's modulus from 26 MPa to 430 MPa–22 MPa and 300 MPa, respectively. While decreased from 645 % to 600 % compared to commercial polyamides, it was due to the fact that sulphur groups within the polyamide backbone hindered the chain packing and constrained the extent of interchain hydrogen bonding. Collectively, these instances clearly demonstrated that thiol-ene click reaction represented a powerful tool for design of "HDPE-like" materials.

Long et al. reported the synthesis of HDPE mimic through chain-transfer ring-opening metathesis polymerization (CT-ROMP) of cyclooctene and hydrogenation to yield carboxytelechelic PE oligomers with various molecular weights. The subsequent polycondensation with diols or diamines produced chain-extended polyesters or polyamides, respectively (Scheme 4b) [66]. These polymers displayed comparable performance to commercial HDPE. Specifically, the polyamides exhibited a T_m ranging from 123 °C to 133 °C and the degree of crystallinity ranging from 46 % to 53 % with increasing the molecular weights of the PE oligomers. Meanwhile, the polyesters also displayed an increase in T_m from 124 °C to 130 °C and an increase in the degree of crystallinity from 53 % to 58 % with increasing PE oligomer length. Additionally, tensile testing of these polyesters and polyamides after chain extension revealed the stress values ranging from 13 MPa to 17 MPa, Young's modulus between 570 MPa and 750 MPa, and strain at break values spanning from 490 % to 1037 %. Similarly, Long et al. produced segmented copolyesters through CT-ROMP and polycondensation of carboxytelechelic PE segments with adipic acid and neopentyl glycol. These copolyesters exhibited more "HDPE-like" properties with increasing PE oligomer length, including the T_m, stress, elongation at break, and Young's modulus, approaching 123 °C, 37 MPa, 380 %, and 820 MPa, respectively [67].

In 2021, Chen and Liu et al. reported the synthesis of polyketones by copolymerization of ethylene and CO with palladium catalyst [69]. The T_m value of the polymer reduced to 147 °C with 24.2 % extra ethylene incorporation. Meantime, Mecking et al. showed that the Ni(II) complexes catalyzed copolymerization of ethylene with CO yielded HDPE mimic with the M_w up to 400 kg/mol and the T_m approaching 134 °C (Fig. 13c), while retaining desirable material properties compared to HDPE [70]. Specifically, these polymers exhibited a Young's modulus of approximately 1062 MPa and a stress of around 26.7 MPa (Fig. 13b). Additionally, the WAXS diffraction patterns of these polymers also showed marked similarity to those of HDPE (Fig. 13a). In parallel, Nozaki et al. reported the synthesis of linear HDPE bearing a low content of ketone groups catalyzed by palladium catalyst [71]. This polymer exhibited the T_m up to 130 °C, effectively preserving a similar thermal property of HDPE (Scheme 4c).

In 2023, Coates et al. proposed the synthesis of polyethylene with double bonds in the polymer backbone using copolymerization of ethylene with an oxa-norbornadiene followed by retro-Diels-Alder reaction. Subsequent cross metathesis with 2-hydroxyethyl acrylate and hydrogenation resulted in ester-capped polyethylene macromonomers. These macromonomers could undergo step growth polymerization to yield HDPE mimics with thermal-mechanical properties comparable to those of commercial HDPE (Scheme 4d). Moreover, T_m values increased from 127.4 °C to 133.9 °C by decreasing the number of ester groups [68].

In summary, a multitude of approaches have been explored to mimic HDPE starting from plant oil feedstock. Indeed, fatty acids are suitable for the design of long-chain aliphatic polymers due to the presence of long chain linear methylene segments. The monomers of



Scheme 4. **a)** The synthesis of sulphur-containing polyamides by thiol-ene click reaction and polycondensation [65]. **b)** The synthesis of carboxy telechelic PE oligomers and the synthesis of chain-extended PEs by polycondensation of carboxy telechelic PE with diol or diamine [66]; **c)** The synthesis of polyketones via ethylene/CO coordination-insertion copolymerization [69–71]; **d)** The synthesis of polyester via retro-Diels-Alder reaction, cross metathesis, hydrogenation and polycondensation [68].

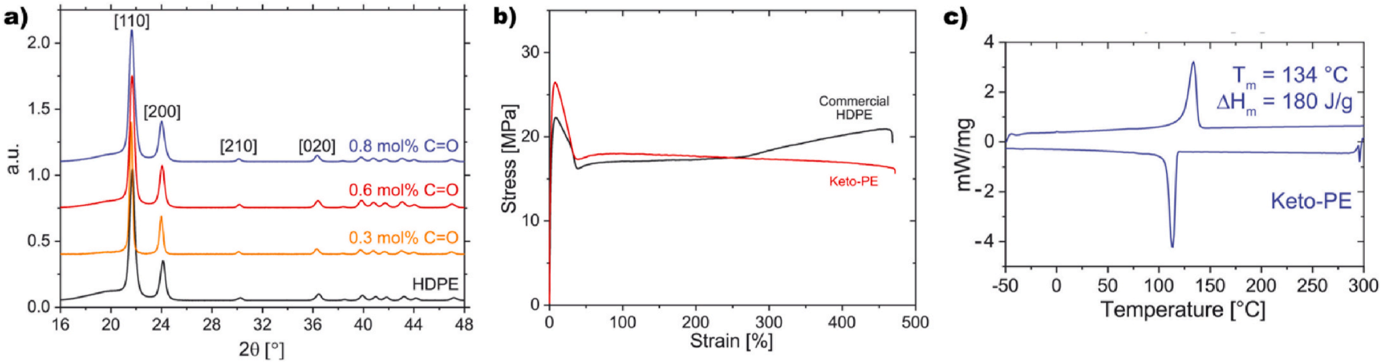


Fig. 13. **a)** WAXS of copolymers with different content of keto; **b)** stress-strain curves of keto-modified HDPE and commercial HDPE; **c)** DSC traces of keto-modified HDPE [70]. Copyright 2021. Adopted with permission from the American Association for the Advancement of Science.

polycondensation are easily derived from plant oils. However, polycondensation reactions entail challenges in controlling molecular weights and dispersity, often demanding high-temperature and vacuum conditions. In contrast, ROP allows for milder conditions while resulting in long-chain aliphatic polymers with high molecular weights. ROMP affords the advantages of generating long-chain aliphatic polymers with random functional group distribution and relatively high molecular weights, although subsequent hydrogenation is necessary for HDPE mimics. Besides, the ring strain is another limitation for the range of cyclic olefins. ADMET proves highly efficient for design of HDPE mimics through either directly polymerization or amalgamation of metathesis reaction with polycondensation. But the drawback of this pathway is the necessary of further hydrogenation steps and the high price of the metathesis catalysts. The thiol-ene reactions expand the database of monomers for other polymerization methods by introducing functional groups into fatty acid derivatives. Additionally, TES polymerization provides an effective method to precisely control the placement of functional groups in the synthesis of HDPE mimics. However, the incorporation of sulphur atoms within the polymer backbone leads to a lower T_m. Various other methods for the synthesis of HDPE mimics have been reported as well, fine-tuning is needed to increase molecular weights, enhance thermos-mechanical properties, and achieve similar crystallinity levels compared to commercial HDPE. The task of elevating molecular weights, improving thermo-mechanical properties, and conducting comprehensive investigations into degradability remains an ongoing pursuit demanding further exploration and scrutiny.

5. Potential new routes

Considering the limitation of these expensive and complicated resources of HDPE mimics, a growing incentive to pursue green bioplastic is also developed from renewable natural resources like plant oils. The main component of plant oils are triglycerides, a class of esters combining glycerol and various fatty acids, such as linolenic acid, linoleic acid, oleic acid, ricinoleic acid, 10-undecenoic acid and erucic acid (Scheme 5a) [55]. The major approach is to prepare linear α, ω-difunctional monomers from fatty acids. For instance, the double bond of oleic acid could be oxidized via ozonolysis to yield azaleic and pelargonic acid in industry [79]. Similarly, the oxidative cleavage can be achieved using tungsten, tantalum, molybdenum, zirconium, and niobium-based catalysts with H_2O_2 in high yield [88,89]. Certain yeast strains like *Candida tropicalis* and *Candida maltose* are able to oxidize terminal aliphatic carbons to carboxylic acids, thereby facilitating the conversion of fatty acids to long-chain dicarboxylic acids [90,91]. Self- or cross-metathesis is another approach to convert the double bonds within unsaturated fatty acids to new linear α, ω-difunctional monomers [80]. A more challenging method is isomerization-functionalization of carbon-carbon double bonds to generate functional groups in the desired terminal positions [54]. Mülhaupt and Mecking et al. reported isomerizing alkoxycarbonylation of methyl oleate and methyl erucate with carbon monoxide and methanol, yielding long-chain diesters for the preparation of long-chain polycondensates (Scheme 5b, Fig. 14a) [48]. All of these approaches provide the possibilities to develop the green bioplastic, with potential utilization of used plant oils as renewable natural resources for the synthesis of “HDPE-like” materials in the near further.

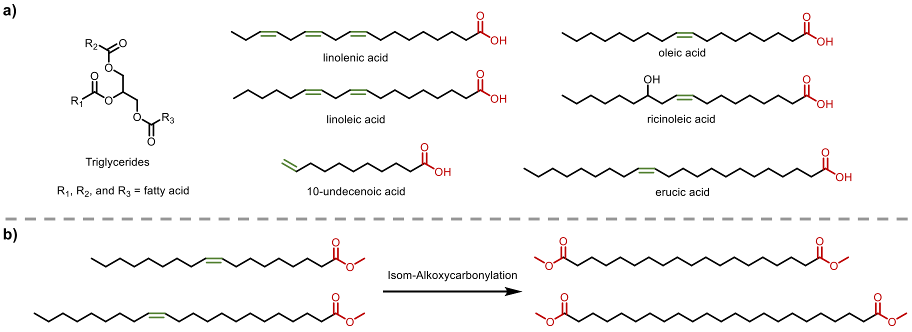
Processing is an effective approach to improving the performance of plant oil-derived bioplastics. Recently, Wang and Tang et al. reported ultra-strong long-chain polyamides via the development of amide diene monomers derived from castor oil, with unidirectional processing (Fig. 14b) [9]. The thermal-mechanical properties and crystallinity of polyamides can be adjusted through monomer feed ratios. Notably, uniaxial deformation resulted in a rearrangement and alignment of crystalline microstructures, achieving an ultrahigh enhancement in mechanical strength.

6. Conclusions and perspectives

Despite the incorporation of degradable functionable groups, including ester, acetal and amide moieties into polyethylene-based backbone being widely explored during the past decade, the realization of sustainable plastic remains a significant challenge. Due to the constrained experimental conditions, many experiments may not be able to attain an industry-level scale-up, where the cost of reactants and catalyst as well as other chemical agents pose significant challenges for the production expenditures. Furthermore, many of these HDPE mimics with added functional groups do not have thermo-mechanical properties consistent with commercial HDPE. Despite this crucial attribute, some studies neglect to characterize the thermo-mechanical characteristics of their HDPE mimics. For some other instances, the repolymerization process could not be successfully completed using the degradable oligomers obtained after chemical degradation. Undoubtedly, these challenges will impede the development of HDPE mimics towards industrial-scale production. Several considerations should be mentioned to address these challenges. First, the thermal and mechanical properties of HDPE mimics should be comparable to those of the commercial counterpart. Second, the cost of HDPE mimics needs to be drastically reduced; it is currently not competitive with commercial HDPE. Third, other physical properties such as gas permeation and chemical resistance, need to be evaluated. Future efforts are encouraged on the synthesis of scalable and low-cost fatty monomers and high molecular weight aliphatic condensation polymers, better and quick analytical tools (i.e. high throughput high temperature GPC), and perhaps utmost the design of highly selective and efficient catalysts for all synthetic processes. It should be considered to explore techno-economic analysis together with life-cycle analysis, should this class of degradable polymers go into large-scale commercialization toward a closed-loop plastic economy.

CRediT authorship contribution statement

Xiaomeng Li: Formal analysis, Methodology, Writing – original draft, Writing – review & editing. **Nagarjuna A. Mahadas:** Formal analysis, Writing – original draft, Writing – review & editing. **Mengxue Zhang:** Formal analysis. **Jacquelyn DePodesta:** Formal analysis. **Morgan Stefik:** Formal analysis, Supervision, Writing – review & editing. **Chuanbing Tang:** Conceptualization, Formal analysis, Funding acquisition, Investigation, Project administration, Supervision, Writing – original draft, Writing – review & editing.



Scheme 5. **a)** A general structure of triglycerides [55]; **b)** Isomerizing alkoxycarbonylation of methyl oleate and methyl erucate [48].

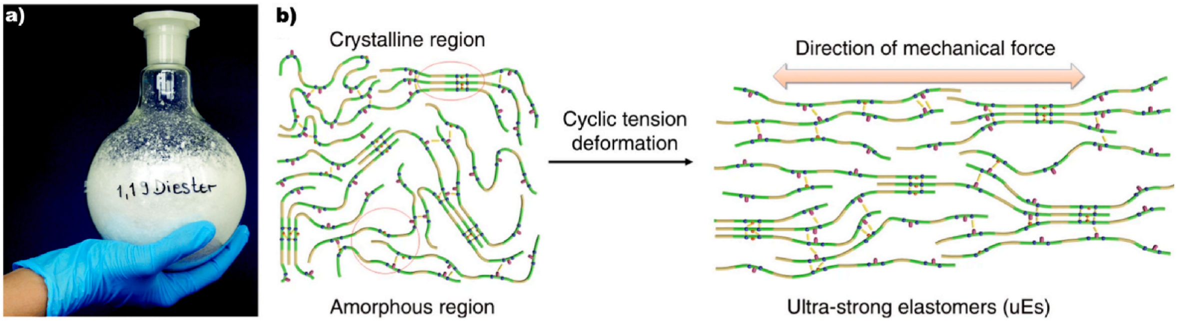


Fig. 14. **a)** Photograph of dimethyl 1,19-nonadecanedioate as obtained from isomerizing methoxycarbonylation of methyl oleate [48]; Copyright 2014. Reprinted with permission from the Royal Society of Chemistry. **b)** A proposed rearrangement of crystalline microstructures via unidirectional cyclic tensile deformation [9]. Copyright 2019. Adopted with permission from Springer Nature.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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References

[1] B. Hu, S. Serranti, N. Fraunholcz, F. Di Maio, G. Bonifazi, Recycling-oriented characterization of polyolefin packaging waste, Waste Manage 33 (3) (2013) 574–584.
[2] OECD, Plastic Pollution Is Growing Relentlessly as Waste Management and Recycling Fall Short, says OECD, 2022. https://www.oecd.org/environment/plastic-pollution-is-growing-relentlessly-as-waste-management-and-recycling-fall-short.htm#:~:text=Plastic%20consumption%20has%20quadrupled%20over%20the%20past%2030. from%202000%20to%202019%20to%20353%20million%20tonnes.).
[3] S.R. Department, Global Plastic Packaging Industry - Statistics & Facts, 2023. https://www.statista.com/topics/10136/plastic-packaging-industry-worldwide/#topicOverview.
[4] Polyolefin Market Size, Share & Trends Analysis Report by Product (Polyethylene, Polypropylene, Polycarbonate), by Application (Film & Sheet, Injection Molding, Blow Molding), by Region, and Segment Forecasts, 2023 - 2033, Grand View Research, 2023.
[5] High Density Polyethylene (HDPE) Market Analysis: Plant Capacity, Production, Process, Technology, Operating Efficiency, Demand & Supply, End-Use, Grade, Foreign Trade, Sales Channel, Regional Demand, Company Share, Manufacturing Process, 2015-2035, Chemanalyst, 2023.
[6] K.O. Babaremu, S.A. Okoya, E. Hughes, B. Tijani, D. Teidi, A. Akpan, J. Igwe, S. Karera, M. Oyinlola, E.T. Akinlabi, Sustainable plastic waste management in a circular economy, Heliyon 8 (7) (2022) e09984.
[7] H.L. Chen, T.K. Nath, S. Chong, V. Foo, C. Gibbins, A.M. Lechner, The plastic waste problem in Malaysia: management, recycling and disposal of local and global plastic waste, SN Appl. Sci. 3 (4) (2021) 437.
[8] I. Vollmer, M.J. Jenks, M.C. Roelands, R.J. White, T. van Harmelen, P. de Wild, G. P. van Der Laan, F. Meirer, J.T. Keurentjes, B.M. Weckhuysen, Beyond mechanical recycling: giving new life to plastic waste, Angew. Chem. Int. Ed. 59 (36) (2020) 15402–15423.
[9] L. Song, T. Zhu, L. Yuan, J. Zhou, Y. Zhang, Z. Wang, C. Tang, Ultra-strong long-chain polyamide elastomers with programmable supramolecular interactions and oriented crystalline microstructures, Nat. Commun. 10 (1) (2019) 1315.
[10] L. Maisonneuve, T. Lebarbé, E. Grau, H. Cramail, Structure–properties relationship of fatty acid-based thermoplastics as synthetic polymer mimics, Polym. Chem. 4 (22) (2013) 5472–5517.
[11] M. Winnacker, Pinenes: abundant and renewable building blocks for a variety of sustainable polymers, Angew. Chem. Int. Ed. 57 (44) (2018) 14362–14371.
[12] M.S. Ganewatta, Z. Wang, C. Tang, Chemical syntheses of bioinspired and biomimetic polymers toward biobased materials, Nat. Rev. Chem 5 (11) (2021) 753–772.
[13] Y. Zhu, C. Romain, C.K. Williams, Sustainable polymers from renewable resources, Nature 540 (7633) (2016) 354–362.
[14] D. Hassanian-Moghaddam, N. Asghari, M. Ahmadi, Circular polyolefins: advances toward a sustainable future, Macromolecules 56 (15) (2023) 5679–5697.
[15] K. Faust, P. Denifl, M. Hapke, Recent advances in catalytic chemical recycling of polyolefins, ChemCatChem (2023) e202300310.
[16] Z.O. Schyns, M.P. Shaver, Mechanical recycling of packaging plastics: a review, Macromol. Rapid Commun. 42 (3) (2021) 2000415.
[17] S.D.A. Sharuddin, F. Abnisa, W.M.A.W. Daud, M.K. Aroua, A review on pyrolysis of plastic wastes, Energy Convers. Manag. 115 (2016) 308–326.
[18] S.C. Kosloski-Oh, Z.A. Wood, Y. Manjarrez, J.P. de Los Rios, M.E. Fieser, Catalytic methods for chemical recycling or upcycling of commercial polymers, Mater. Horiz. 8 (4) (2021) 1084–1129.
[19] Q. Hou, M. Zhen, H. Qian, Y. Nie, X. Bai, T. Xia, M. Laiq Ur Rehman, Q. Li, M. Ju, Upcycling and catalytic degradation of plastic wastes, Cell Rep. Phys. Sci. 2 (8) (2021) 100514.
[20] K. Faust, P. Denifl, M. Hapke, Recent advances in catalytic chemical recycling of polyolefins, ChemCatChem 15 (13) (2023) e202300310.
[21] Z.R. Hinton, M.R. Talley, P.A. Kots, A.V. Le, T. Zhang, M.E. Mackay, A. M. Kunjapur, P. Bai, D.G. Vlachos, M.P. Watson, M.C. Berg, T.H. Epps, L.T. J. Korley, Innovations toward the valorization of plastics waste, Annu. Rev. Mater. Res. 52 (1) (2022) 249–280.
[22] K. Ragaert, L. Delva, K. Van Geem, Mechanical and chemical recycling of solid plastic waste, Waste Manage 69 (2017) 24–58.
[23] H. Chen, K. Wan, Y. Zhang, Y. Wang, Waste to wealth: chemical recycling and chemical upcycling of waste plastics for a great future, ChemSusChem 14 (19) (2021) 4123–4136.
[24] M. Solis, S. Silveira, Technologies for chemical recycling of household plastics – a technical review and TRL assessment, Waste Manage 105 (2020) 128–138.
[25] J. Alvarez, S. Kumagai, C. Wu, T. Yoshioka, J. Bilbao, M. Olazar, P.T. Williams, Hydrogen production from biomass and plastic mixtures by pyrolysis-gasification, Int. J. Hydrogen Energy 39 (21) (2014) 10883–10891.
[26] G. Lopez, A. Erkiaga, M. Artetxe, M. Amutio, J. Bilbao, M. Olazar, Hydrogen production by high density polyethylene steam gasification and in-line volatile reforming, Ind. Eng. Chem. Res. 54 (39) (2015) 9536–9544.
[27] I. Ahmad, M.I. Khan, H. Khan, M. Ishaq, R. Tariq, K. Gul, W. Ahmad, Pyrolysis study of polypropylene and polyethylene into premium oil products, Int. J. Green Energy 12 (7) (2015) 663–671.
[28] A. Arroyave, S. Cui, J.C. Lopez, A.L. Kocen, A.M. LaPointe, M. Delferro, G. W. Coates, Catalytic chemical recycling of post-consumer polyethylene, J. Am. Chem. Soc. 144 (51) (2022) 23280–23285.
[29] A. Piovano, E. Paone, The reductive catalytic upcycling of polyolefin plastic waste, Curr. Res. Green Sustain. Chem. 5 (2022) 100334.
[30] S.S. Borkar, R. Helmer, F. Mahnaz, W. Majzoub, W. Mahmoud, M.m. Al-Rawashdeh, M. Shetty, Enabling resource circularity through thermo-catalytic and solvent-based conversion of waste plastics, Chem Catal. 2 (12) (2022) 3320–3356.
[31] D. Munir, M.F. Irfan, M.R. Usman, Hydrocracking of virgin and waste plastics: a detailed review, Renewable Sustainable Energy Rev. 90 (2018) 490–515.
[32] C.S. Costa, H.D. Thi, K.M. Van Geem, M.R. Ribeiro, J.M. Silva, Assessment of acidity and the zeolite porous structure on hydrocracking of HDPE, Sustain. Energy Fuels 6 (15) (2022) 3611–3625.
[33] S. Liu, P.A. Kots, B.C. Vance, A. Danielson, D.G. Vlachos, Plastic waste to fuels by hydrocracking at mild conditions, Sci. Adv. 7 (17) (2021) eabf8283.
[34] B.C. Vance, P.A. Kots, C. Wang, J.E. Granite, D.G. Vlachos, Ni/SiO2 catalysts for polyolefin deconstruction via the divergent hydrogenolysis mechanism, Appl. Catal., B 322 (2023) 122138.
[35] F. Zhang, M. Zeng, R.D. Yappert, J. Sun, Y.-H. Lee, A.M. LaPointe, B. Peters, M. M. Abu-Omar, S.L. Scott, Polyethylene upcycling to long-chain alkylaromatics by tandem hydrogenolysis/aromatization, Science 370 (6515) (2020) 437–441.
[36] G. Celik, R.M. Kennedy, R.A. Hackler, M. Ferrandon, A. Tennakoon, S. Patnaik, A. M. LaPointe, S.C. Ammal, A. Heyden, F.A. Perras, M. Pruski, S.L. Scott, K. R. Poeppelmeier, A.D. Sadow, M. Delferro, Upcycling single-use polyethylene into high-quality liquid products, ACS Cent. Sci. 5 (11) (2019) 1795–1803.
[37] I.L. Peczak, R.M. Kennedy, R.A. Hackler, R. Wang, Y. Shin, M. Delferro, K. R. Poeppelmeier, Scalable synthesis of Pt/SrTiO3 hydrogenolysis catalysts in pursuit of manufacturing-relevant waste plastic solutions, ACS Appl. Mater. Interfaces 13 (49) (2021) 58691–58700.

[38] C. Jia, S. Xie, W. Zhang, N.N. Intan, J. Sampath, J. Pfaendtner, H. Lin, Deconstruction of high-density polyethylene into liquid hydrocarbon fuels and lubricants by hydrogenolysis over Ru catalyst, Chem Catal. 1 (2) (2021) 437–455.

[39] Y. Nakaji, M. Tamura, S. Miyaoka, S. Kumagai, M. Tanji, Y. Nakagawa, T. Yoshioka, K. Tomishige, Low-temperature catalytic upgrading of waste polyolefinic plastics into liquid fuels and waxes, Appl. Catal., B 285 (2021) 119805.

[40] M. Tamura, S. Miyaoka, Y. Nakaji, M. Tanji, S. Kumagai, Y. Nakagawa, T. Yoshioka, K. Tomishige, Structure-activity relationship in hydrogenolysis of polyolefins over Ru/support catalysts, Appl. Catal., B 318 (2022) 121870.

[41] A.S. Goldman, A.H. Roy, Z. Huang, R. Ahuja, W. Schinski, M. Brookhart, Catalytic alkane metathesis by tandem alkane dehydrogenation-olefin metathesis, Science 312 (5771) (2006) 257–261.

[42] M.C. Haibach, S. Kundu, M. Brookhart, A.S. Goldman, Alkane metathesis by tandem alkane-dehydrogenation–olefin-metathesis catalysis and related chemistry, Acc. Chem. Res. 45 (6) (2012) 947–958.

[43] Z. Huang, E. Rolfe, E.C. Carson, M. Brookhart, A.S. Goldman, S.H. El-Khalafy, A.H. R. MacArthur, Efficient heterogeneous dual catalyst systems for alkane metathesis, Adv. Synth. Catal. 352 (1) (2010) 125–135.

[44] X. Jia, C. Qin, T. Friedberger, Z. Guan, Z. Huang, Efficient and selective degradation of polyethylenes into liquid fuels and waxes under mild conditions, Sci. Adv. 2 (6) (2016) e1501591.

[45] R.J. Conk, S. Hanna, J.X. Shi, J. Yang, N.R. Ciccia, L. Qi, B.J. Bloomer, S. Heuvel, T. Wills, J. Su, A.T. Bell, J.F. Hartwig, Catalytic deconstruction of waste polyethylene with ethylene to form propylene, Science 377 (6614) (2022) 1561–1566.

[46] N.M. Wang, G. Strong, V. DaSilva, L. Gao, R. Huacuja, I.A. Konstantinov, M. S. Rosen, A.J. Nett, S. Ewart, R. Geyer, S.L. Scott, D. Guironnet, Chemical recycling of polyethylene by tandem catalytic conversion to propylene, J. Am. Chem. Soc. 144 (40) (2022) 18526–18531.

[47] M. Hong, E.Y.X. Chen, Completely recyclable biopolymers with linear and cyclic topologies via ring-opening polymerization of γ-butyrolactone, Nat. Chem. 8 (1) (2016) 42–49.

[48] F. Stempfle, B.S. Ritter, R. Mülhaupt, S. Mecking, Long-chain aliphatic polyesters from plant oils for injection molding, film extrusion and electrospinning, Green Chem. 16 (4) (2014) 2008–2014.

[49] A.G. Pemba, J.A. Flores, S.A. Miller, Acetal metathesis polymerization (AMP): a method for synthesizing biorenewable polyacetals, Green Chem. 15 (2) (2013) 325–329.

[50] P.H. Nguyen, S. Spoljaric, J. Seppälä, Redefining polyamide property profiles via renewable long-chain aliphatic segments: towards impact resistance and low water absorption, Eur. Polym. J. 109 (2018) 16–25.

[51] M. Winnacker, B. Rieger, Biobased polyamides: recent advances in basic and applied research, macromol, Rapid Commun 37 (17) (2016) 1391–1413.

[52] O. Türünç, M.A.R. Meier, Fatty acid derived monomers and related polymers via thiol-ene (click) additions, Macromol. Rapid Commun. 31 (20) (2010) 1822–1826.

[53] Y. Xia, X. Yue, Y. Sun, C. Zhang, X. Zhang, Chemically recyclable polyethylene-like sulfur-containing plastics from sustainable feedstocks, Angew. Chem. Int. Ed. 62 (13) (2023) e202219251.

[54] F. Stempfle, P. Ortmann, S. Mecking, Long-chain aliphatic polymers to bridge the gap between semicrystalline polyolefins and traditional polycondensates, Chem. Rev. 116 (7) (2016) 4597–4641.

[55] Z. Wang, M.S. Ganewatta, C. Tang, Sustainable polymers from biomass: bridging chemistry with materials and processing, Prog. Polym. Sci. 101 (2020) 101197.

[56] F. Stempfle, P. Ortmann, S. Mecking, Which polyesters can mimic polyethylene? Macromol. Rapid Commun. 34 (1) (2013) 47–50.

[57] M. Häußler, M. Eck, D. Rothauer, S. Mecking, Closed-loop recycling of polyethylene-like materials, Nature 590 (7846) (2021) 423–427.

[58] F. Stempfle, D. Quinzler, I. Heckler, S. Mecking, Long-chain linear C19 and C23 monomers and polycondensates from unsaturated fatty acid esters, Macromolecules 44 (11) (2011) 4159–4166.

[59] D. Myers, T. Witt, A. Cyriac, M. Bown, S. Mecking, C.K. Williams, Ring opening polymerization of macrolactones: high conversions and activities using an yttrium catalyst, Polym. Chem. 8 (37) (2017) 5780–5785.

[60] M.P.F. Pepels, M.R. Hansen, H. Goossens, R. Duchateau, From polyethylene to polyester: influence of ester groups on the physical properties, Macromolecules 46 (19) (2013) 7668–7677.

[61] T. Haider, O. Shyshov, O. Suraeva, I. Lieberwirth, M. von Delius, F.R. Wurm, Long-chain polyorthoesters as degradable polyethylene mimics, Macromolecules 52 (6) (2019) 2411–2420.

[62] P. Ortmann, S. Mecking, Long-spaced aliphatic polyesters, Macromolecules 46 (18) (2013) 7213–7218.

[63] J. Trzaskowski, D. Quinzler, C. Bährle, S. Mecking, Aliphatic long-chain C20 polyesters from olefin metathesis, Macromol. Rapid Commun. 32 (17) (2011) 1352–1356.

[64] P. Ortmann, I. Heckler, S. Mecking, Physical properties and hydrolytic degradability of polyethylene-like polyacetals and polycarbonates, Green Chem. 16 (4) (2014) 1816–1827.

[65] P.H. Nguyen, S. Spoljaric, J. Seppälä, Renewable polyamides via thiol-ene 'click' chemistry and long-chain aliphatic segments, Polymer 153 (2018) 183–192.

[66] A.S. Arrington, T.E. Long, Influence of carboxytelechelic oligomer molecular weight on the properties of chain extended polyethylenes, Polymer 259 (2022) 125319.

[67] A.S. Arrington, J.R. Brown, M.S. Win, K.I. Winey, T.E. Long, Melt polycondensation of carboxytelechelic polyethylene for the design of degradable segmented copolyester polyolefins, Polym. Chem. 13 (21) (2022) 3116–3125.

[68] S.M. Parke, J.C. Lopez, S. Cui, A.M. LaPointe, G.W. Coates, Polyethylene incorporating diels–alder comonomers: a "trojan horse" strategy for chemically recyclable polyolefins, Angew. Chem. Int. Ed. 62 (30) (2023) e202301927.

[69] S.-Y. Chen, R.-C. Pan, M. Chen, Y. Liu, C. Chen, X.-B. Lu, Synthesis of nonalternating polyketones using cationic diphosphazane monoxide-palladium complexes, J. Am. Chem. Soc. 143 (28) (2021) 10743–10750.

[70] M. Baur, F. Lin, T.O. Morgen, L. Odenwald, S. Mecking, Polyethylene materials with in-chain ketones from nonalternating catalytic copolymerization, Science 374 (6567) (2021) 604–607.

[71] S. Tang, F.W. Seidel, K. Nozaki, High density polyethylenes bearing isolated in-chain carbonyls, Angew. Chem. Int. Ed. 60 (51) (2021) 26506–26510.

[72] X.-Y. Wang, Y. Gao, Y. Tang, Sustainable developments in polyolefin chemistry: progress, challenges, and outlook, Prog. Polym. Sci. 143 (2023) 101713.

[73] M.G. Menges, J. Penelle, C. Le Fevere de Ten Hove, A.M. Jonas, K. Schmidt-Rohr, Characterization of long-chain aliphatic polyesters: crystalline and supramolecular structure of PE22,4 elucidated by X-ray scattering and nuclear magnetic resonance, Macromolecules 40 (24) (2007) 8714–8725.

[74] P. Yuan, Y. Sun, X. Xu, Y. Luo, M. Hong, Towards high-performance sustainable polymers via isomerization-driven irreversible ring-opening polymerization of five-membered thionolactones, Nat. Chem. 14 (3) (2022) 294–303.

[75] C. Shi, R.W. Clarke, M.L. McGraw, E.Y.X. Chen, Closing the "one monomer–two polymers–one monomer" loop via orthogonal (De)polymerization of a lactone/olefin hybrid, J. Am. Chem. Soc. 144 (5) (2022) 2264–2275.

[76] A. Lv, Z.-L. Li, F.-S. Du, Z.-C. Li, Synthesis, functionalization, and controlled degradation of high molecular weight polyester from itaconic acid via ADMET polymerization, Macromolecules 47 (22) (2014) 7707–7716.

[77] H. Mutlu, L.M. de Espinosa, M.A.R. Meier, Acyclic diene metathesis: a versatile tool for the construction of defined polymer architectures, Chem. Soc. Rev. 40 (3) (2011) 1404–1445.

[78] K.B. Wagener, J.M. Boncella, J.G. Nel, Acyclic diene metathesis (ADMET) polymerization, Macromolecules 24 (10) (1991) 2649–2657.

[79] M.A.R. Meier, J.O. Metzger, U.S. Schubert, Plant oil renewable resources as green alternatives in polymer science, Chem. Soc. Rev. 36 (11) (2007) 1788–1802.

[80] L. Montero de Espinosa, M.A.R. Meier, Plant oils: the perfect renewable resource for polymer science? Eur. Polym. J. 47 (5) (2011) 837–852.

[81] C. Zhang, T.F. Garrison, S.A. Madbouly, M.R. Kessler, Recent advances in vegetable oil-based polymers and their composites, Prog. Polym. Sci. 71 (2017) 91–143.

[82] X. Zhang, M. Fevre, G.O. Jones, R.M. Waymouth, Catalysis as an enabling science for sustainable polymers, Chem. Rev. 118 (2) (2018) 839–885.

[83] S. Chikkali, S. Mecking, Refining of plant oils to chemicals by olefin metathesis, Angew. Chem. Int. Ed. 51 (24) (2012) 5802–5808.

[84] M. Eck, S.T. Schwab, T.F. Nelson, K. Wurst, S. Iberl, D. Schleheck, C. Link, G. Battagliarin, S. Mecking, Biodegradable high-density polyethylene-like material, Angew. Chem. Int. Ed. 62 (6) (2023) e202213438.

[85] J. Cai, C. Liu, M. Cai, J. Zhu, F. Zuo, B.S. Hsiao, R.A. Gross, Effects of molecular weight on poly(ω-pentadecalactone) mechanical and thermal properties, Polymer 51 (5) (2010) 1088–1099.

[86] C. Liu, F. Liu, J. Cai, W. Xie, T.E. Long, S.R. Turner, A. Lyons, R.A. Gross, Polymers from fatty acids: poly(ω-hydroxyl tetradecanoic acid) synthesis and physico-mechanical studies, Biomacromolecules 12 (9) (2011) 3291–3298.

[87] H. Mutlu, M.A.R. Meier, Unsaturated PA X,20 from renewable resources via metathesis and catalytic amidation, Macromol. Chem. Phys. 210 (12) (2009) 1019–1025.

[88] H. Noureddini, M. Kanabur, Liquid-phase catalytic oxidation of unsaturated fatty acids, J. Am. Oil Chem. Soc. 76 (3) (1999) 305–312.

[89] E. Antonelli, R. D'Aloisio, M. Gambaro, T. Fiorani, C. Venturello, Efficient oxidative cleavage of olefins to carboxylic acids with hydrogen peroxide catalyzed by methyltrioctylammonium tetrakis(oxodiperoxotungsto)phosphate(3−) under two-phase conditions. Synthetic aspects and investigation of the reaction course, J. Org. Chem. 63 (21) (1998) 7190–7206.

[90] S. Zibek, W. Wagner, T. Hirth, S. Rupp, S. Huf, Fermentative Herstellung der α,ω-Dicarbonsäure 1,18-Oktadecendisäure als Grundbaustein für biobasierte Kunststoffe, Chem. Ing. Tech. 81 (11) (2009) 1797–1808.

[91] S. Huf, S. Krügener, T. Hirth, S. Rupp, S. Zibek, Biotechnological synthesis of long-chain dicarboxylic acids as building blocks for polymers, Eur. J. Lipid Sci. Technol. 113 (5) (2011) 548–561.