

Chemically Recyclable Polyolefin Mimics

‘Synthesis, Characterization and Application of Polyethylene-like
Polyesters’

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‘If I have seen further it is by standing on the shoulders of Giants.’

Isaac Newton

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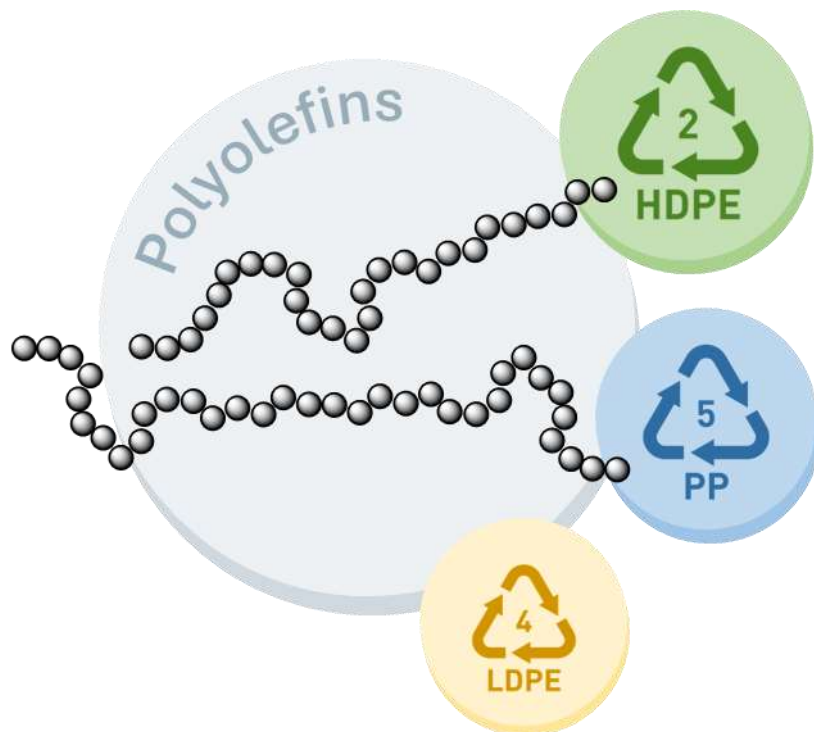
ADMET	acyclic diene metathesis	LSAPE	long-spaced aliphatic polyesters
ADP	acceptorless dehydrogenative polymerization	MAO	methylaluminoxane
AI	artificial intelligence	M_e	entanglement molecular weight
ALCPE	aliphatic long-chain polyester	MFR	melt flow rate
APR	aqueous phase reforming	M_n	number average molecular weight
BTX	benzene, toluene, xylene	M_w	weight average molecular weight
CAM	cross-alkane metathesis	NHC	<i>N</i> -heterocyclic carbene complex
CCTP	coordinative chain transfer polymerization	NIR	near-infrared
cROP	catalytic ring-opening polymerization	OBC	olefin block copolymer
CSP	chain shuttling polymerization	PBD	polybutadiene
CTA	chain transfer agent	PBS	polybutylene succinate
<i>d</i>	density	PBT	poly(butylene terephthalate)
$\bar{D}_M$	dispersity	PCR	post-consumer resin
DHIP	diethyl 5-(hydroxymethyl) isophthalate	PET	polyethylene terephthalate
DIE	dehydrogenation and isomerizing ethenolysis	PGA	polyglycolic acid
EPDM	ethylene propylene diene monomer	PHP	poly(H-phosphonate)
EPR	ethylene propylene rubber	PLA	polylactic acid
EVA	ethylene-vinyl acetate copolymer	POE	polyolefin elastomer
FFF	fused filament fabrication	PPDL	polypentadecalactone
HAT	hydrogen atom transfer	PPO	poly(phenylene oxide)
HDPE	high density polyethylene	PS	polystyrene
<i>i</i> PP	isotactic polypropylene	PTFE	polytetrafluoroethylene
Ir-POCOP	iridium-based pincer ethylene complex	PVC	polyvinyl chloride
<i>l</i>	lamellar thickness	R	ideal gas constant
LCB	long chain branching	ROMP	ring-opening metathesis polymerization
LDPE	low density polyethylene	ROP	ring-opening polymerization
LLDPE	linear low-density polyethylene	S_NAr	aromatic substitution
		SSC	single-site catalyst
		T_c	ceiling temperature
		TEM	transmission electron microscopy
		TETA	2,4,6-triethoxy-1,3,5- triazine
		T_g	glass transition temperature

T_m	melting temperature	X_E	mole fraction of ester groups
TPO	thermoplastic polyolefin		
Tri-HDI	tris(6isocyanatohexyl) isocyanurate	XLPE	cross-linked polyethylene
		ΔG_m	Gibbs free energy of mixing
UHMWPE	ultra-high molecular weight polyethylene	ΔH_m	enthalpy of fusion
		ε	thermal energy penalty
WAXS	wide-angle X-ray scattering	ε_b	elongation at break
α	number of segments in polymer	σ	surface free energy
		χ	interaction parameter
X_c	crystallinity level	ϕ	volume fraction

CHAPTER I

Introduction

This chapter discusses the success story and dominance of polyolefins in the global market, current state of polyolefin-based waste management, as well as the limitations of the established recycling strategies.



1. Introduction

An undeniable success story of synthetic polymers began in the mid-20th century following the accidental discovery of low-density polyethylene, which quickly accelerated a wave of landmark breakthroughs in polyolefin development.¹⁻³ These pioneering breakthroughs fundamentally shaped the modern polymer era, laying the foundation for the contemporary global plastics industry. Decades of research and innovation afforded a plethora of polymers with tunable molecular weights, topology, composition and functionality, making them often the first-choice materials in both low-value and high-performance applications.^{4,5} As of now, it is nearly impossible to imagine present day world without plastics, as they penetrated almost every aspect of our daily life – from single-use packaging, construction, electronics, healthcare to agriculture. Among the vast diversity of macromolecular architectures, one group of polymers stands out as the undisputed cornerstone of the global plastics market – polyolefins, which due to their combination of cost-efficiency and functional versatility maintain a dominant position with about half of global market share.^{6,7} The solely aliphatic hydrocarbon backbone of polyolefins provides apolar, durable, chemically stable and lightweight materials. Yet, the same properties that make polyolefins so unique contribute to their limited miscibility with other polymers and resilience against environmental decomposition. Furthermore, the chemical and thus spectroscopic similarity of various polyolefin grades often preclude effective automated sorting, fundamentally limiting the purity and quality of post-consumer recyclates.⁸ While polyolefins were originally designed for long-term stability, their primary application as single-use packaging contributes to large volumes of plastic waste and growing pollution. Despite the alarming and well-documented ecological risks, the global pathways for tackling plastic waste still rely on landfilling and incineration. Current plastic waste management strategies are far from perfect, as recirculation remains challenging due to the inefficient sorting of mixed materials, which ultimately compromises the solid-state properties of recyclates.⁹ To mitigate the negative footprint of linearity of plastics, future polymer systems should be redesigned in a manner that grants reusability and recyclability. The pursuit of more sustainable alternatives to conventional synthetic plastics has prompted a shift toward the concept of circular polyolefins, balancing the high performance and end-of-life deconstructability.

1.1 A brief history of polyolefins

Throughout history, the progress of human civilizations has been inseparably linked to the evolution of materials, spanning from natural materials like wood, leather, through metal alloys and glass up to precisely designed polymers. While mastering the application of traditional materials had been gradually refined over centuries, the discovery of vulcanized natural rubber in 1844 started a material revolution of so far unmet scale (Figure 1.1).^{10, 11} A major milestone occurred in 1907 when Leo Baekland developed the first synthetic phenol-formaldehyde resin, which due to its rigidity, heat and electrical resistance was used in molded castings and insulators.^{12, 13} The groundwork for this emerging field of chemistry was laid in the 1920s, when Hermann Staudinger formulated the concept of polymers – high molecular weight macromolecules composed of covalently linked monomers (*gr. polus meros* ‘many parts’).¹⁴ It took years for Staudinger’s revolutionary concept to be understood, but the impact of his work was eventually honoured in 1953 with the Nobel Prize in Chemistry.^{15, 16} The demand for lightweight, functional, affordable and durable materials intensified, also driven by the growing need for innovative wartime solutions. In 1933 researchers from Imperial Chemical Industries (ICI) from England investigated high-pressure polymerization of ethylene, which serendipitously led them to the discovery of low-density polyethylene (LDPE).³ Interestingly, similar white waxy substance had already been produced in 1898 by von Pechmann, however, the use of industrially unfavorable diazomethane hampered the concept for years.¹⁷ Only after Perrin (ICI) managed to tame and reproduce the high-pressure reaction did the industrial scale production of LDPE begin in 1939. The combination of short- and long-chain branching within LDPE provides low density and melting point along with enhanced flexibility, high melt strength and ductility, essential for film-blowing application.¹⁸

Between the 1930s to 1950s the discovery of novel synthetic polymers rocketed, with PET, nylon, PTFE, silicones and polyurethanes evolving as the most significant examples, all of which remain relevant today.¹⁹ In early 1950s, John Hogan and Robert Banks from Phillips Petroleum employed chromium trioxide supported on silica as a catalyst for synthesis of polyethylene. The Phillips process allowed polyethylene to be synthesized under milder conditions, making industrial-scale production both practical and cost-effective.²⁰ Subsequently, in 1953 Karl Ziegler discovered a titanium-based heterogeneous catalytic system capable of polymerizing ethylene into linear, highly crystalline and tough, high-density polyethylene (HDPE).¹ Ziegler’s invention soon gained momentum within the research

community and caught the attention of Giulio Natta, who in 1954 utilized the catalyst for other α -olefins like propene. This led to the milestone discovery of isotactic polypropylene (iPP) – a strong material with highly packed crystalline structure and first-ever controlled stereochemistry of polymer chain.^{2, 21, 22} Ziegler and Natta were jointly awarded the Nobel Prize in 1963 for their work ‘*in the field of the chemistry and technology of high polymers*’, a breakthrough that not only revolutionized organometallic chemistry but also paved the ways for the massive industrial-scale production of commodity plastics that defined the modern era.^{23, 24}

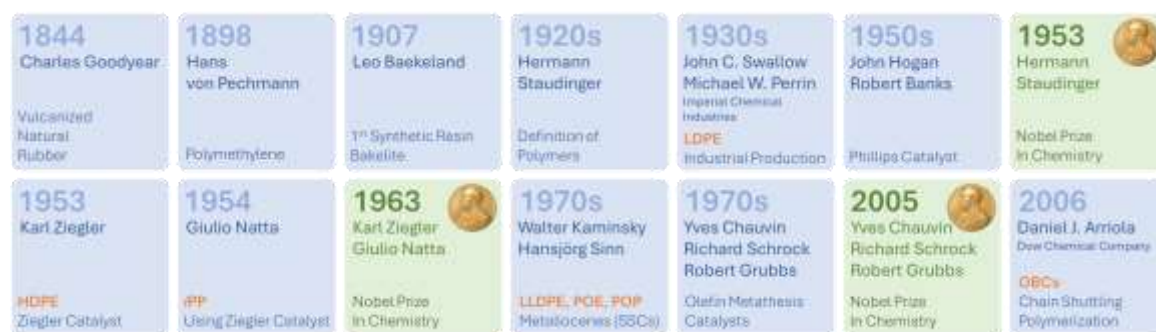


Figure 1.1. Timeline of the most important discoveries and innovations in polyolefin history.

The relatively brief 10-year interval between two Nobel Prizes, awarded within the rapidly growing field of polymer chemistry, exemplifies the dynamic evolution and significance of these materials in a post-war world. In the 1970s, the demand for advanced polyolefins with tailored mechanical properties induced the development of more robust and versatile catalytic architectures (Figure 1.2). Walter Kaminsky and Hansjörg Sinn investigated systems based on metallocenes of group 4 transition metals (Ti, Zr, Hf) activated with methylaluminumoxane (MAO), what enabled the stereoselective copolymerization of ethylene and propylene with numerous α -olefins (but-1-ene, hex-1-ene, oct-1-ene).²⁵ Single-site catalysts (SSCs) allow for the synthesis of numerous polymers with uniform comonomer incorporation and narrow molecular weight distributions, where the final material properties are precisely tuned by adjusting the symmetry of the metallocene ligands.²⁶ Consequently, Kaminsky’s innovation facilitated the design of novel polyolefin topologies, including linear low-density polyethylene (LLDPE), high-performance polyolefin elastomers (POE) based on ethylene and higher α -olefins, along with thermoplastic polyolefins (TPO) comprising a PP matrix combined with elastomeric components (EPR, EPDM).

Concurrently, the research community explored whether functional, heteroatom containing groups could be incorporated directly into the polymer backbone, challenging the limitation of technologies solely compatible with non-polar hydrocarbon monomers. In the early 1970s, Yves Chauvin established the theoretical explanation for the olefin

metathesis by proposing the metal-carbene [2+2] cycloaddition mechanism, which provided the crucial foundation for the subsequent development of highly potent catalytic systems.²⁷ Building upon Chauvin's work, Richard Schrock and Robert Grubbs pioneered the development of well-defined organometallic compounds, which eventually allowed for the controlled polymerization of monomers containing various chemical functionalities.²⁸⁻³⁰ While Schrock-type catalysts were based on early transition metals like molybdenum and tungsten (Mo, W),³¹ Grubbs systems contained late transition metals, most notably ruthenium (Ru).³² The significantly lower oxophilicity of Ru center renders Grubbs' catalysts far more tolerant to heteroatom-containing functional groups, as well as less sensitive to water and oxygen. The mechanistic understanding of olefin metathesis, along with the successive development of several metathesis catalysts (Schrock, 1st and 2nd generation Grubbs, Hoveyda-Grubbs), has allowed the conversion of both acyclic and cyclic olefins into precisely controlled architectures.^{33, 34} Specifically, the use of ring-opening metathesis polymerization (ROMP) and acyclic diene metathesis (ADMET) has facilitated the design of functionalized polyolefins with a previously unattainable degree of control. In 2005, Chauvin, Schrock and Grubbs were jointly awarded the Nobel Prize in Chemistry for their contribution to "*the development of the metathesis method in organic synthesis*".³⁵

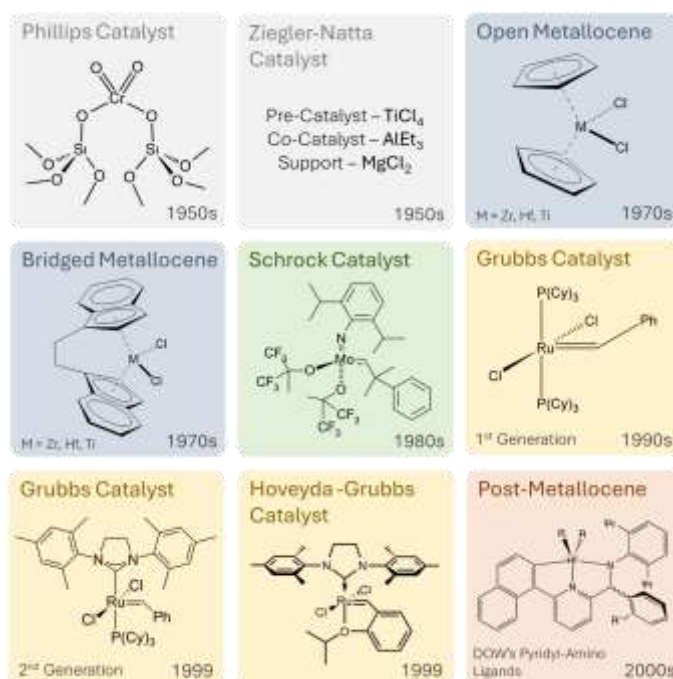


Figure 1.2. Chronological evolution of polyolefin catalysis, illustrating the transition from heterogeneous Phillips and Ziegler-Natta systems to single-site catalysts and post-metallocenes.

One of the most recent advancements in polyolefin technology was the development of olefin block copolymers (OBCs) by Dow Chemical Company in 2006 via chain shuttling polymerization.^{36, 37} By applying a dual-catalyst system (post-metallocenes) mediated by a chain shuttling agent (Et_2Zn), where each of catalysts has a preference towards incorporation of linear (*hard*) or branched (*soft*) segment, this process provides multiblock architectures. Contrary to random copolymers, OBCs combine the higher thermal resistance of linear polyethylenes with the low-temperature elasticity of highly branched polyolefins.

In conclusion, the first decades of polyolefin science focused on the rapid industrialization of Ziegler-Natta technology, eventually leading to mass-scale production of commodity plastics. The 1970s marked the beginning of new era characterized by the development of highly active and well-defined catalytic systems, which allowed precise control over the polymer's topology. It is truly exceptional that with just a handful of simple monomers, such vast array of polymer architectures can be achieved. Over the years, due to the versatility and unrivaled cost-to-performance ratio, the global polyolefin market has grown exponentially, reaching a value of nearly \$263 billion in 2024.⁷ Though polyolefins cemented a dominant position within the global economy, the increasing plastic waste crisis has caused a paradigm shift within the research community – the 21st century necessitates a transition from environmentally persistent to degradable by design materials.

1.2 Current state of polyolefin market

1.2.1 Global polyolefin market

While the mass production of plastics started in mid-20th century, it was the post-World War II industrial growth that intensified global polymer manufacturing. The explosion in plastic production was the result of technological, industrial and societal factors, where catalytic innovation, cost-efficiency and increasing demand of consumer goods fueled this unprecedented growth. Between 1950 to 2015, plastic production reached 8.3 billion metric tons, with more than half of this volume generated in the last two decades alone.⁶ The industrial dominance of polyolefins is reflected by the fact that they make up nearly 60% of globally mass-produced plastics, highlighting their critical role within plastic economy.^{7, 38} The global polyolefin market is estimated to reach \$358 billion by 2030, growing at a compound annual growth rate (CAGR) of 5.4% between 2025 – 2030.⁷ Based on the most recent market analysis from 2024, polyethylene (PE) and polypropylene (PP) accounted for the largest revenue share share of 37.4% and 27.0%, consecutively.⁷ The remaining market

share is distributed among ethylene-vinyl acetate copolymer (EVA) and specialty polyolefin thermoplastics, such as polyolefin elastomers, which are expected to grow significantly owing to a versatile performance profile that balances mechanical and thermal resilience, easy processability and structural tunability.⁷ According to 2025 market reports, the Asia-Pacific region, led primarily by China, dominates global polyolefin production accounting for approximately 50% of global business.³⁹ While strict regulatory changes, energy costs and economic instabilities that Europe is currently facing lead to plant closures and marginal growth, the expansion of polyolefin industry in Asia is driven by beneficial policies and regulatory changes, along with new investments and rapid socioeconomic development.⁴⁰⁻
⁴⁴ Since 2022 Europe has become a net importer of plastics, mainly from United States, South Korea, China and Saudi Arabia, broadening its overdependency of crucial materials and products.³⁹ As European plastics industry suffers from decreasing competitiveness, it remains fundamental to ensure production and protect European manufacturing supply chains.³⁹



Figure 1.3. Primary characteristics and major industrial applications of commodity polyolefins.⁹

The versatility of polyolefins stems from the tunability of their physicochemical properties via the control of molecular weight, branching topology and chain tacticity and sequence distribution. This structural adjustability allows for the synthesis of a vast array of optimized architectures precisely designed to fulfill the technical requirements of numerous applications (Figure 1.3). The packaging sector represents the dominant market for polyolefins, enclosing a vast spectrum from rigid containers and flexible films to non-woven medical textiles.⁴⁵⁻⁴⁷ Their cost-effectiveness, mechanical integrity and inherent chemical inertness have made polyolefins fundamental for single-use application. Despite their industrial utility, the application of such persistent materials in single-use framework creates a profound

environmental risk, as the average service life of 6 months accounts for the accumulation of massive waste volumes.^{6, 48} The second largest market for polyolefins is construction and infrastructure, where their chemical inertness and lightweightness offer significant advantages over traditional materials (steel, concrete) by lowering the installation and long-term maintenance costs.^{49, 50} The automotive and transportation sector represents the third ranking market for polyolefins, where they serve a critical function in vehicle's weight optimization.⁵¹ By substituting conventional materials used for interior and exterior vehicle's components – such as steel and rubber – with lightweight polyolefins, manufacturers significantly reduce its weight, thus optimizing fuel consumption and lowering carbon emissions.

1.2.2 Classification of commodity polyolefins

Within the polyethylene family, the main classification is established on density, a macroscopic property that directly reflects the branching frequency and subsequent degree of crystallinity (Figure 1.4).⁵² Starting at the upper limit of the density gradient, HDPE comprises linear chains that promotes efficient lamellar packing within a characteristic orthorhombic unit cell. The absence of significant branching leads to high density ($d = 0.94 - 0.98 \text{ g/cm}^3$) and high degree of crystallinity reaching up to $X_c = 80\%$.⁵³ These structural features translate to high thermal stability, with melting points around $135 \text{ }^\circ\text{C}$, and low glass transition ($T_g \sim -115 \text{ }^\circ\text{C}$), ultimately providing a mechanically superior balance between stiffness and ductility. The low molecular weight between entanglements ($M_e = 1250 - 1760 \text{ g/mol}$) provides a cohesive and robust network, as high entanglement density remains critical for polymer's ductility and ultimate tensile strength.⁵⁴ Ultra-high molecular weight polyethylene (UHMWPE) resins represent a subgroup of HDPE with weight-average molecular weight (M_w) exceeding $3 \cdot 10^6 \text{ g/mol}$.^{52, 53, 55} Such high molecular weight in combination with a high entanglement density provide unprecedented impact strength, low coefficient of friction, self-lubrication and abrasion resistance superior to that of steel. Though its extremely high viscosity precludes conventional manufacturing via melt processing techniques, UHMWPE can be (i) molded, sintered and machined into its final shape (prosthetics, bearings, high performance materials); (ii) gel-spun into high strength fibers (*Dyneema*®, DSM).^{56, 57}

Controlled copolymerization of ethylene and an α -olefin (1-butene, 1-hexene, 1-octene) yields linear low-density polyethylene (LLDPE) with tunable concentration of short-chain branches, thus providing materials with broader density range of $0.85 - 0.93 \text{ g/cm}^3$.⁵⁸ Typically, commercial LLDPEs comprise $8 - 12 \text{ wt}\%$ of comonomer and relatively narrow molecular

weight distribution, resulting in lower melting points and overall crystallinity than HDPE (115 – 125 °C). The industrial importance of LLDPE in the flexible packaging sector (plastic wraps, liners, geomembranes, tubing) is attributed to its superior puncture and environmental stress cracking resistance combined with high extensibility. These properties are a direct consequence of its short-chain branching, which translates to lower melt-strength and lower shear-thinning behavior, providing ability to downgauge while preserving high strength.

Another compelling commercial polyolefin platform centers on ethylene-propylene copolymers, broadly classified as ethylene-propylene rubber (EPR) (30 – 60 wt% of C₃). Tunability is the hallmark of these systems: systematically adjusting the ethylene-to-propylene ratio yields a diverse spectrum of amorphous to semi-crystalline polymers equipped with exceptional thermal stability, electrical insulation, and photostability. Incorporating a trace non-conjugated diene, such as an ethylidene norbornene or dicyclopentadiene unit, introduces crosslinkable sites that enable sulfur vulcanization, converting the linear chains into robust ethylene-propylene-diene monomer (EPDM) elastomers.⁵⁸

Unlike HDPE or LLDPE, low density polyethylene (LDPE), produced via high-pressure, free-radical polymerization, has long-chain branching (LCB) hampering tight crystal packing. Consequently, LDPE is distinguished by reduced crystallinity, melting point (105 – 120 °C) and compromised density of 0.91 – 0.93 g/cm³.^{52, 58} This branched architecture inherently reduces the crystal size, offering an optically transparent material. Though LDPE possesses lower tensile strength than HDPE and LLDPE, the presence of LCB provides exceptional melt strength essential for blown film extrusion.

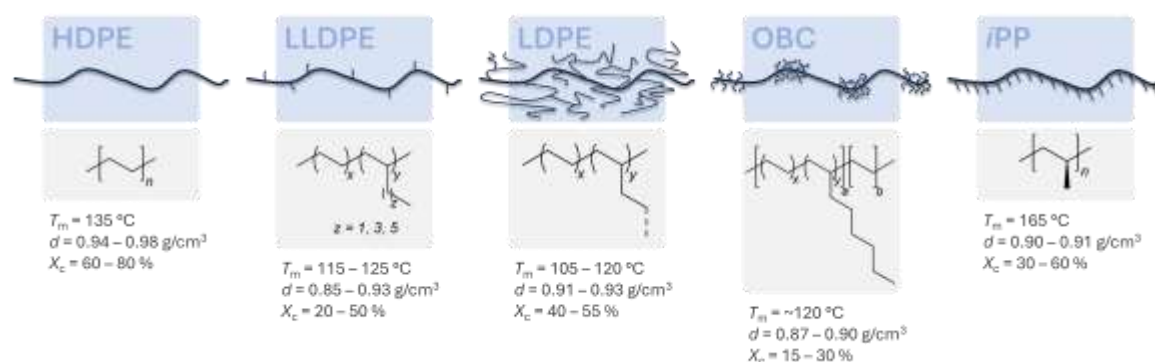


Figure 1.4. Structures of commodity polyolefins HDPE, LLDPE, LDPE, OBC and iPP and their characteristic properties.⁵⁹

Revolutionary Chain Shuttling Polymerization (CSP) allows for the synthesis of segmented olefin block copolymers (OBC), distinctive from random ethylene and α -olefin copolymers.^{36,}

⁶⁰ Through the use of binary catalyst system and chain shuttling agent, these materials

effectively incorporate alternating hard crystalline blocks (toughness) and soft amorphous blocks (elasticity). Such topology allows OBCs to maintain the high melting point (~ 120 °C) even when the total crystallinity is reduced, whereas random copolymers suffer from a simultaneous decline in both T_m and X_c . Concurrently, the density of olefin block copolymers spans from 0.87 to 0.90 g/cm³, being dictated by the content of the amorphous soft segments.⁶¹ As a result, at elevated temperatures they tend to hold their shape better than LLDPE or POE, offering a superior high-temperature elastic recovery combined with low-temperature impact toughness, making them perfect for hygiene products, hot melt adhesives and footwear.

Isotactic polypropylene (*i*PP) is characterized by monoclinic α -form crystal structure and has lower density ($d = 0.90 - 0.91$ g/cm³) and crystallinity level (30 – 60%) than HDPE.^{3, 59} Nonetheless, *i*PP has significantly higher melting points (~ 165 °C) and glass transition temperature around 0 °C. Thus, it remains tough and resistant to higher temperatures, but brittle, especially within lower temperature region. It is worth noting that the crystalline form of PP depends heavily on the rates of crystalline nucleation, which controlled by the cooling rate, ultimately governs the density, crystallinity degree and mechanical performance. Since processing conditions can induce metastable crystalline structures (α , β , γ) in the solid state^{62, 63}, nucleating agents (sodium benzoate, phosphate esters, minerals, sorbitols) are usually added to boost the crystallization of the material.⁶⁴ To improve the toughness and impact properties of polypropylene essential for low-temperature performance, a small fraction of ethylene is typically introduced. Heat resistance of *i*PP enables it to be used as medical and laboratory devices, as well as food containers, as it can be sterilized and won't melt upon hot filling. High rigidity and fatigue resistance make *i*PP perfect for piping systems, automotive parts and plastic hinge applications.⁶⁵ Polypropylene can be also drawn into stain-resistant fibers for sanitary, hygiene, clothing and upholstery applications.⁶⁶

1.3 Recycling strategies for polyolefins

The primary monomers for polyolefin synthesis, ethylene and propylene, are predominantly derived from fossil fuel feedstock. Consequently, conventional commodity thermoplastics often exhibit significant environmental persistence, though emerging design strategies can impart degradability. They are neither biodegradable nor susceptible to mild chemical deconstruction, as the high dissociation energies of their apolar C–C and C–H bonds create a challenging kinetic barrier to deconstruction.^{67, 68} Historically, the petrochemical sector

was considered as a secondary consumer of fossil resources. As of 2013, plastics production accounted for approximately 7% of annual oil consumption.^{69, 70} However, as the global transportation sector shifts towards electrification and renewable resources, the strategic focus of oil companies has pivoted. Current forecasts indicate that the reliance on fossil fuel feedstocks for petrochemicals will continue to grow.^{71, 72}

One might naturally consider the transition to more environmentally friendly bioplastics as a panacea for rising dependency on petroleum-derived materials. However, to what extent can bioplastics indeed serve as an alternative to traditional polyolefins? While bioplastics are frequently proposed as a solution to plastic pollution, they currently represent a marginal 1% of global production, with growth hampered by increasing costs and technical limitations.^{39, 47, 70, 73, 74} Additionally, “*biobased*” does not inherently imply “*biodegradable*”. For instance, bio-polyethylene synthesized from sugarcane-derived ethylene is chemically indistinguishable from its conventional analogue. Consequently, despite its green origination and lower carbon footprint, bio-polyethylene remains non-biodegradable and faces the same end-of-life challenges as fossil-based polyolefins.^{75, 76} Secondary, it remains unclear whether consumers are willing to accept the green alternatives, especially considering their compromised performance to cost ratio relative to commodity polyolefins. Recent consumer surveys unequivocally indicate that while sustainability of packaging is perceived as a fundamental factor, there is lack of willingness to pay premium for greener alternatives, what again reinforces the dominance of cost-efficient polyolefins.⁷⁷

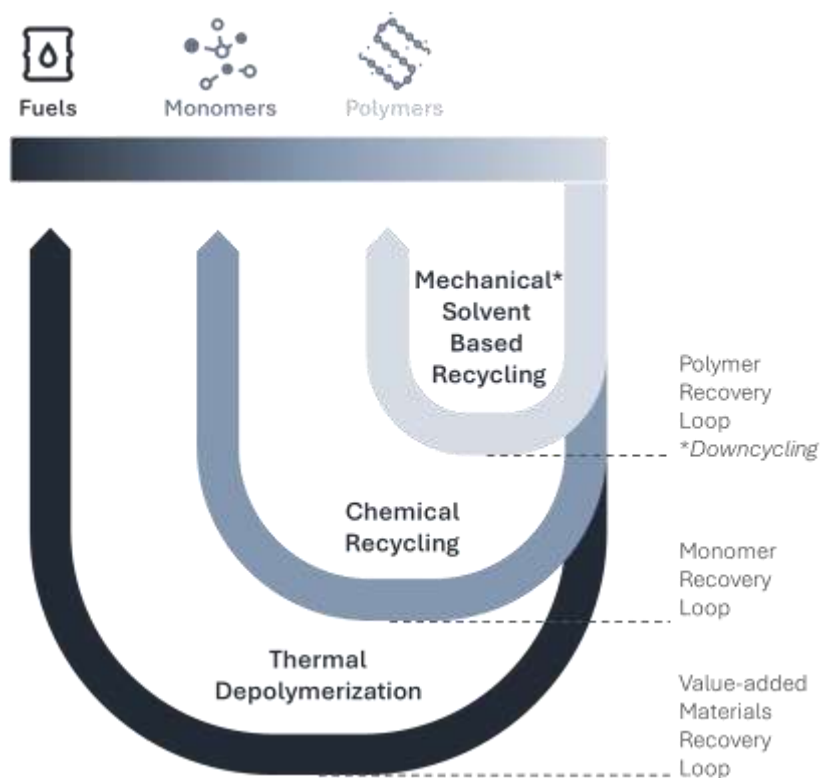


Figure 1.5. Main polyolefin recycling pathways.

Contrary to common perception, upon closer examination of their lifecycle, polyolefins emerge as one of the most sustainable polymeric materials.⁴ The implementation of commodity plastics in modern infrastructure plays a crucial role in global resource management. These materials not only secure the food supply chain but also contribute to energy savings through thermal insulation of buildings and transportation-related reductions in fuel use and carbon emissions. Large-scale polyolefin manufacturing fulfills all demands of green chemistry, including lack of solvents, ambient reaction conditions, minute by-product and waste generation, as well as catalytic, non-toxic, safe production and reasonable recycling strategies when available in pure form (e.g. HDPE milk jugs, LLDPE post-industrial recyclates).^{4, 69, 78} Purely hydrocarbon backbone of polyolefins allows for the conservation of high energy in stable, transportable and lightweight form, while requiring less energy for production relative to metals and ceramics.⁶⁹ This energy can be later reclaimed through multiple pathways: melt-state reprocessing provides secondary life of existing resins (mechanical recycling), while controlled thermochemical degradation enables the near-quantitative recovery of virgin-quality chemical feedstocks (chemical recycling and catalytic deconstruction) (Figure 1.5).

The American Society for Testing and Materials (ASTM) has categorized various methods of plastic recycling into four types: primary, secondary, tertiary and quaternary, as defined

by ASTM D5033-00.⁷⁹ Primary recycling involves the thermal reprocessing of pristine, undegraded plastic waste streams (e.g. disposables), whereas secondary recycling refers to extrusion of degraded plastics and mixed waste streams. These processes cannot maintain the properties of virgin plastics, resulting in downcycling. Tertiary recycling involves converting post-consumer polymer waste into raw chemicals or original monomers, which often offers a closed-loop economy strategy. Quaternary recycling refers to incineration of plastic waste. The novelisations of these definitions (ISO15270, ASTM D7209-06) group primary and secondary recycling as mechanical recycling, tertiary recycling as chemical and quaternary recycling as incineration. All recycling methods are prioritized in a strict hierarchy, with primary recycling ranking highest due to its minimal energy consumption and ability to preserve original polymer properties.

1.3.1 The global status of polymer recycling

Cumulative data spanning from 1950 to 2015 reveals that a mere 9% of globally produced polymers have been recycled, with only 10% of that fraction undergoing more than one recycling cycle (Figure 1.6).⁶ While recycling rates vary significantly across different polymers, with polyethylene terephthalate (PET) and HDPE exhibiting the highest rates due to more established collection infrastructures, they remain alarmingly low for the broader spectrum of materials. Beyond mechanical recovery of post-consumer materials, incineration accounts for the treatment of 12% of plastic waste. However, this pathway is criticized for its significant carbon footprint and the potential of release of hazardous emissions, presenting a compromise between energy recovery and environmental toxicity. The remaining fraction of global plastic production – approximately 79% – is discarded, leading to vast accumulation in landfills and permeation to natural ecosystems. Both on land and in marine ecosystems, the inertness of plastics prevents degradation and mineralization, leading instead to physical erosion and the formation of micro- and nanoplastics, which not only accumulate in the environment, but enter global food chain and thus human body posing unknown long-term health risks.⁸⁰⁻⁸²

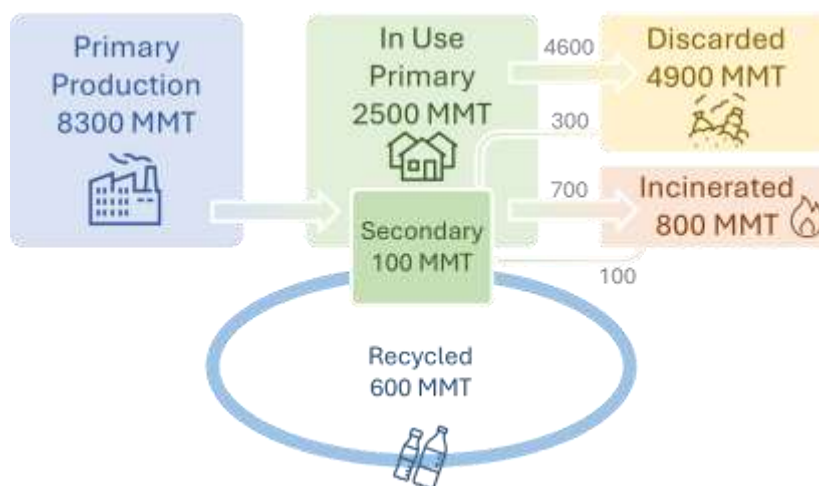


Figure 1.6. Global production and use of polymer resins from 1950 to 2015.⁶

By 2022, the global fraction of landfilled plastic waste decreased to approximately 40%, driven mainly by China’s strategic shift from landfilling toward air-controlled incineration, where 60% of waste undergoes thermal degradation. Similarly, Japan (70%) and European Union (38%) prioritized “*zero-landfill*” strategy, gravitating toward energy-from-waste technologies as a primary method for plastic waste management.⁷¹ Despite a measurable shift in environmental consciousness and an increased awareness of the negative effects of polymer waste, global recycling rates remain alarmingly low. Technical and economic barriers to recycling, such as efficient collection and sorting of polymer waste and unmatched cost-effectiveness of pristine plastics compared with post-consumer resins, continue to stagnate recovery rates.

1.3.2 Mechanical recycling

Mechanical recycling remains the most prevalent, economically viable, and environmentally benign method for polymer waste reclamation (Figure 1.7). The production of high-purity, homogenous post-consumer resins (PCR), of sufficient quality to withstand subsequent compounding and melt-reprocessing, necessitates a rigorous, multistep preparation: (1) sorting and separation, (2) size reduction via shredding or milling, (3) contaminant removal, and (4) washing and drying.^{79, 83} Despite these established protocols, the efficient separation of polymer waste from non-plastic fractions (glass, metal, paper, wood), followed by the sorting of discrete polymer species, remains a significant challenge. Current industrial sorting infrastructures rely on physical differences in size and weight (e.g. films vs bottles), density (e.g. PET vs PE/PP) and near-infrared (NIR) spectral signatures.⁸⁴ Magnetic separators are typically integrated to reclaim ferrous metals (e.g. steels, iron), while

ballistic separators and wind shifters sort materials based on their size. Density-based separation, utilizing hydrocyclones, sink float techniques and vibrational tables, is highly effective for broad compositions but is limited when density ranges overlap. Examples include LLDPE and LDPE, talcum-filled PP and PS or PET and PVC.⁸⁵ In such instances, NIR spectroscopy technologies are indispensable, often augmented by artificial intelligence (AI) and machine learning algorithms for pattern recognition. Each polymer class possesses a unique NIR fingerprint, where characteristic vibrational bands indicate specific functional groups. These on-line registered spectra trigger pneumatic nozzles to eject target materials from the conveyor belt with high precision. However, in the specific case of polyolefins, the NIR spectra are highly similar due to their nearly identical hydrocarbon backbones, frequently leading to limited sorting efficiency.



Figure 1.7. Industrial workflow for the sorting and mechanical recycling of post-consumer plastic waste.

Following successful isolation, high quality post-consumer resins are reprocessed into granules via melt-extrusion. This solvent free, highly scalable approach has gained significant industrial dominance due to high throughput and economic efficiency.⁷⁹ However, during melt processing, polymers are subjected to high heat and mechanical shear, which inevitably triggers thermomechanical degradation. In the presence of oxygen, these elevated temperatures and stresses initiate oxidation, leading to the formation of macroradicals. These reactive species subsequently undergo chain scission or cross-linking side reactions. Consequently, repeatedly recycled materials often exhibit compromised mechanical, optical and thermal properties, failing to meet the performance requirements for virgin resins. The degradation mode is highly dependent on the polymer class and processing parameters, rendering the final properties of the recyclate inconsistent.⁸⁶ In the case of HDPE, chain scission initially dominates, yet prolonged thermo-oxidation induces long chain branching and eventual cross-linking, which increases melt viscosity.⁸⁷ Conversely, isotactic polypropylene is susceptible to shear-induced radical formation at the tertiary carbon, resulting in chain scission. This leads to a reduction in molecular weight

and a corresponding increase in the melt flow rate (MFR), yielding a low-viscosity material.⁸⁸ As a result, the performance gap between virgin and recycled resins often restricts their applicability to lower-value “*downcycled*” applications. Recent technoeconomic analyses of mechanical recycling across a spectrum of polymers indicate that recyclates remain economically uncompetitive when compared with their pristine counterparts since their market viability depends on government subsidies or dramatic rise in crude oil prices.⁸⁹

A more sophisticated form of mechanical recycling that currently gains more industrial attention is solvent based recycling, also referred to as dissolution-precipitation methods. In this process, polymer waste is dissolved in solvents without altering the macromolecular architecture, enabling the high-selectivity separation of mixed streams from additives, pigments and contaminants yielding virgin-quality products.^{90, 91} The primary technologies for solvent-based recycling are: (1) solvent-antisolvent purification, (2) temperature-swing method, and (3) supercritical solvent method. The first technique employs a selective solvent that dissolves the target polymer, followed by the introduction of an antisolvent triggering the rapid phase separation and precipitation of the polymer from the solution.⁹² Temperature-swing method relies on the inherent temperature-dependent solubility of polymers, where controlled cooling induces the precipitation of selected stream.⁹³ Finally, a supercritical solvent strategy requires the use of solvents in their supercritical state, where slight manipulations of temperature and pressure govern the resulting solubility parameters.⁹⁴ These recycling methods are particularly interesting as they provide high-quality recyclates and allow recycling of industrially difficult, multi-layered packaging, yet the energy requirements, large-scale solvent handling and recovery continue to be challenging.⁹⁵

A further critical limitation inherent to mechanical recycling is the cross-contamination of polymer streams, which results in the formation of immiscible blends characterized by poor mechanical performance. For instance, despite the structural similarities between polypropylene and polyethylene, they are thermodynamically immiscible.^{96, 97} Thus, inclusion of even a small fraction of one as a contaminant leads to phase-separated morphologies and diminished tensile strength. These shortcomings can be mitigated with compatibilizers, which typically have an amphiphilic architecture demonstrating affinity for both phases at the interface. The most prominent polyolefin compatibilizers include block and graft copolymers, polyolefin elastomers, and olefin block copolymers, as well as semi-crystalline polyesters.^{59, 98} As the third chapter of this work explores the recycling of polyethylene-like polyesters, a comprehensive review of the relevant literature regarding blend compatibilization will be detailed in that section.

1.3.3 Chemical recycling

Contrary to mechanical recycling, chemical recycling deconstructs polymers into oligomers, small molecules including monomers, thereby preserving high product quality and supporting the objectives of closed-loop circular economy.^{79,99,100} For polymers containing cleavable functional groups (e.g. PET, polyesters, polyamides), this is typically achieved via solvolysis. These processes are named after the specific cleaving molecules, such as hydrolysis, alcoholysis, glycolysis, and effectively regenerate monomeric units or low molecular weight oligomers.¹⁰¹ However, polyolefins lack these hydrolyzable functional groups. Consequently, their chemical recycling is primarily performed via thermolysis, wherein valuable chemical feedstocks are yielded only at elevated temperatures. As chain-growth polymers, polyolefins are fundamentally enthalpy-driven. They possess a high ceiling temperature ($T_c \sim 400 - 600\text{ }^\circ\text{C}$), marking the thermodynamic threshold at which depolymerization becomes favorable.¹⁰² The thermal decomposition of polyolefins requires the cleavage of C–C and C–H bond, followed by the formation of reactive alkyl radicals. These species propagate via chain-end β -scission, backbiting and intermolecular radical transfer, also referred to as random scissions (Figure 1.8). While chain-end scission leads to the release of unsaturated monomers from the radical terminus, random scissions primarily yield oligomeric fractions. The process eventually terminates through radical recombination or disproportionation.¹⁰³ Interestingly, the least stable C–C bonds are those whose cleavage yields resonance-stabilized radicals, such as the benzyl radicals and allyl radicals in polystyrene (PS) and polybutadiene (PBD), respectively. Despite its all-carbon backbone, PS weakened tertiary carbon bonds promote thermal unzipping to afford high monomer yields ($\sim 70\%$), while in case of PBD lighter products are formed at the same temperature compared to other polyolefins.¹⁰⁴ Nonetheless, the resulting product is governed by reaction temperature, residence time and reactor geometry, which dictates the heat transfer efficiency. Yet, these high-temperature radical processes suffer from competing side reactions that generate a wide range of undesired byproducts, including light gases, aromatics, waxes and char. Furthermore, similar to mechanical reprocessing, the presence of additives, fillers, and contaminants can hamper decomposition efficiency and generate potentially toxic residues. Thus, rigorous segregation into homogenous waste streams is often required to prevent the synthesis of mixed, low-value feedstocks that necessitate uneconomical purification steps.¹⁰⁴

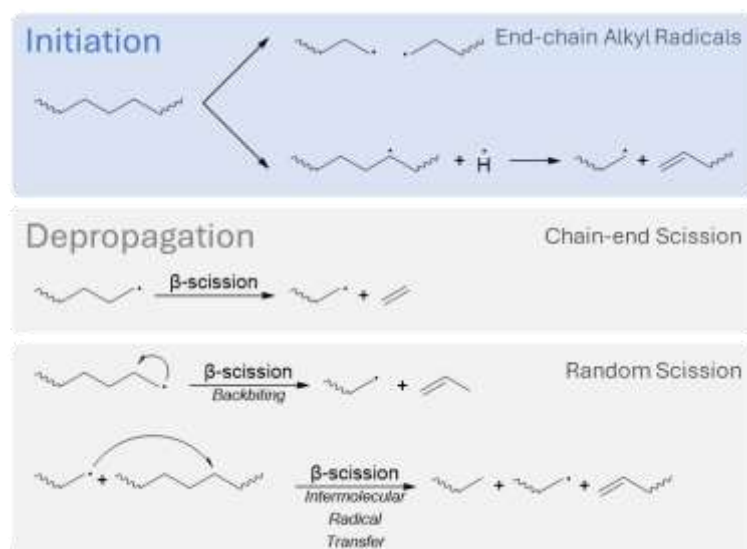


Figure 1.8. Initiation and depropagation mechanisms in polyolefin thermolysis.

Pyrolysis is an emerging thermochemical recycling process with significant commercial potential, though it is still operating at a relatively modest scale. It involves the thermal degradation of plastics in the absence of oxygen at temperatures exceeding the ceiling temperature, yielding a range of petrochemical feedstocks including light gases such as ethylene, propylene (closed-loop recycling), liquid fuels, naphtha and waxes (open-loop recycling). The product distribution is highly sensitive to kinetic parameters: shorter residence times combined with lower temperatures ($\sim 500\text{ }^{\circ}\text{C}$) promote random scission pathways, predominantly yielding waxy paraffinic products (Figure 1.8). Conversely, elevating the temperature to $800\text{ }^{\circ}\text{C}$ favors end-chain scission, leading to higher recovery rates of ethylene and propylene.⁹⁹ Further increases in residence time and temperature shift the equilibrium toward the formation of mono- and polycyclic aromatic hydrocarbons via complex side reactions including Diels-Alder cyclization.¹⁰⁵ Pyrolysis is particularly advantageous for recycling mixed waste streams that are unsuitable for mechanical recycling. In this process, non-volatile additives and contaminants are isolated as a solid residue (char), which requires separate disposal. However, the resulting pyrolysis products often necessitate further post-hydrotreatment and purification to meet the industrial specifications, as they frequently exhibit higher sulfur and nitrogen contents compared to conventional liquid fuels.

An advanced iteration, hydropyrolysis, utilizes a pressurized hydrogen atmosphere as the reaction medium. Consequently, alkyl radicals undergo chain transfer to H_2 , and unsaturated bonds are hydrogenated, resulting in a product mixture composed primarily of saturated hydrocarbons.¹⁰⁶ While this pathway precludes the direct recovery of ethylene and propylene monomers, hydropyrolysis effectively hampers the formation of char

and aromatics, yielding a cleaner, more stable liquid fuel fraction. Given that polyolefins are derived from fossil-based feedstocks, their carbon to hydrogen (C : H) ratio remains equivalent to that of conventional transportation fuels, such as gasoline, diesel and kerosene. As a consequence, the conversion of polyolefin waste into pyrolysis oil for use as a liquid fuel represents a primary objective for majority of current recycling technologies. Beyond its application as a direct fuel source, pyrolysis oil can be further refined or upgraded into value-added oxygenated chemicals, such as alcohols and aldehydes, or catalytically reformed to BTX aromatics (benzene, toluene, xylene).¹⁰⁷

Gasification of both homo- and heterogenous plastic waste is conducted at temperatures exceeding 1000 °C in the presence of a controlled amount of oxidizing agent, such as steam, oxygen or air. This process yields synthetic gas (syngas), a mixture composed of hydrogen (H₂) and carbon monoxide (CO).¹⁰⁸ The major advantage of gasification lies in the production of this well-defined chemical product: H₂ : CO ratio determines the feasibility of subsequent syntheses, including the production of basic chemicals, including methanol and ammonia, or synthetic fuels via Fischer-Tropsch processes.⁷⁹ Gasification can be implemented as a standalone technology or as a secondary stage following pyrolysis, where the resulting solid char is utilized as a substrate for syngas production. During the gasification process, the fragmented polymer chains undergo a sequence of partial oxidation, dry reforming, steam reforming and partial combustion. Ultimately, both pyrolysis and gasification are projected to remain the dominant thermochemical recycling technologies for the foreseeable future, owing to their operational flexibility, feedstock tunability and favorable industrial economics.⁹⁹

1.3.4 Catalytic deconstruction

To overcome the inherent lack of selectivity and intensive energy demands of pyrolysis and gasification, catalytic deconstruction pathways have emerged as a more precise, energy-efficient alternative for polyolefin recycling (Figure 1.9).¹⁰⁹ By employing heterogenous or homogenous catalysts, the activation energy for C – C bond cleavage is significantly reduced, shifting the degradation mechanisms from radical pathways to controlled ionic or organometallic cycles. These catalytic methodologies enable operation at moderate temperatures up to 300 °C, addressing the critical need for industrially viable controlled recycling pathways under mild conditions.¹¹⁰

One of the primary technologies is the catalytic hydrocracking of polyolefins, typically utilizing bifunctional catalysts that comprise both metallic and acidic sites, most commonly

including Pt, Ru, Co supported on different zeolites.¹⁰⁹ The mechanism of hydrocracking under mild temperatures proceeds through a sequence: (1) initial dehydrogenation to form unsaturated double bonds, (2) skeletal isomerisation at the acidic sites followed by chain cleavage via carbenium-ion pathways, and (3) final hydrogenation of the resulting olefins. This approach degrades the polymer chains more efficiently, leading to high yields of C₅ – C₁₂ liquid fractions suitable for gasoline-grade feedstocks.^{111, 112}

In contrast, hydrogenolysis generally employs monofunctional metal catalysts on supports, (e.g. Ru, Pt, Ni and Zr).¹¹³ In this pathway, both the hydrogen and the polyolefin backbone are co-adsorbed on the metallic active sites. This adsorption facilitates the scission of H – H and C – C bonds, subsequently leading to the formation of terminal C – H bonds and shorter hydrocarbon chains.¹¹² Compared to hydrocracking, hydrogenolysis typically requires longer reaction times and exhibits slightly diminished throughput. However, it is highly effective at producing heavier, diesel grade hydrocarbons (C₉ – C₂₂).¹¹¹

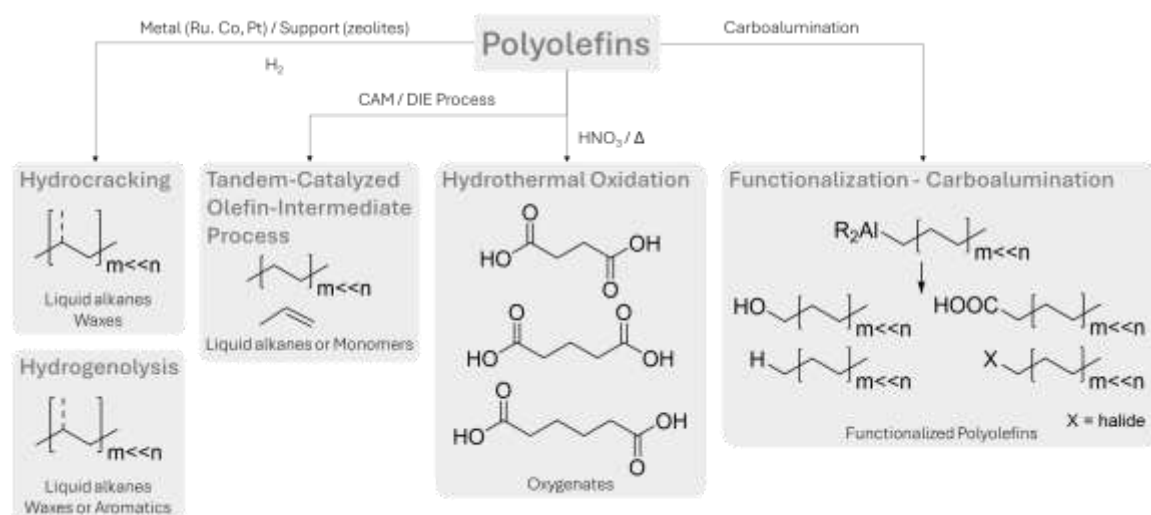


Figure 1.9. Strategies for catalytic chemical recycling of polyolefins.¹⁰⁹

A further approach gaining significant academic interest implements tandem strategies that involve olefin intermediates to upcycle polyolefin waste into high-value hydrocarbon feedstocks.^{114, 115} One of the most prominent pathways is tandem catalytic cross-alkane metathesis (CAM), which employs a dual-catalysts system: an iridium-based pincer complex ([Ir]) and heterogeneous Re₂O₇/γ-Al₂O₃ catalyst. In this cycle, [Ir] complex facilitates the initial dehydrogenation of both the polyolefin and the solvent (e.g. *n*-hexane).^{116, 117} The resulting unsaturated species undergo metathesis reaction at the rhenium sites, effectively fragmenting the polymer chains. These shortened chains are subsequently re-hydrogenated by the [Ir] catalyst to yield liquid alkanes. In some instances, these strategies have been

successfully applied to post-consumer resins, as exemplified by dehydrogenation and isomerizing ethenolysis (DIE).¹¹⁸ In this multi-stage process, an [Ir] complex and *tert*-butylethylene in *p*-xylene produce a partially dehydrogenated polyethylene. This intermediate is subsequently subjected to metathesis using a Grubbs-Hoveyda catalyst under an ethylene atmosphere, followed by isomerization via a palladium (Pd) catalyst. The controlled isomerization of internal double bonds toward the terminal olefins ultimately yields propylene. Numerous iterations of this tandem process exist, varying in reaction conditions (100 – 300 °C), residence times and catalyst selections (Sn, Pt, Re, W, Ru, or Grubbs catalyst).^{109, 119-121} Depending on the selected protocol, these systems can be tuned to produce either light alkanes or α -olefins, the latter of which provides a direct route for repolymerization back into virgin-quality polymers.

While the aforementioned methodologies primarily yield saturated and unsaturated hydrocarbon fractions, emerging strategies focus on the open-loop recycling of polyolefin waste into oxygenated, value-added chemicals. By employing specific catalytic systems, the degradation process can be precisely navigated toward controlled oxidation, preventing the slow environmental decomposition or the uncontrolled combustion to CO₂ typical for incineration. A prominent approach involves the oxidative degradation of polyethylene in diluted nitric acid (HNO₃) at 180 °C.¹²² This process enables the formation of small-chain organic acids, such as dicarboxylic succinic and glutaric acid. These oxygenated intermediates can be further refined via catalytic decarboxylation, using either electro- or photocatalytic pathways, to generate gaseous hydrocarbons, light olefins and carbon dioxide.¹²³ Similarly, hydrothermal oxidation of polyethylene waste under mild conditions (aqueous H₂O₂ at 200 °C) yields a mixture of small carboxylic acids and CO₂. These can subsequently be subjected to aqueous phase reforming (APR) over Ru or Ru-Ni catalysts on mesoporous carbon, generating hydrogen gas as a sustainable energy carrier.¹²⁴ Beyond simple oxidation, the functionalization of the inert hydrocarbon backbone of polyolefins can be achieved through catalytic C – C cleavage and alumination. The supported organozirconium catalysts cleave and transform the polymer chains into alkylaluminum intermediates. Such reactive species can subsequently react with various electrophiles to provide a vast array of functionalized products, ranging from fatty alcohols, carboxylic acids to alkyl halides, effectively repurposing waste polyolefins into high-value chemical building blocks.^{125, 126}

1.4 Aim and outline of this thesis

While state-of-the-art thermochemical and mechanical recycling technologies continue to address legacy waste streams, conventional polyolefins, the largest class of synthetic polymers, remain inherently difficult to recycle without performance degradation or high energy demands. To overcome these fundamental limits, a paradigm shift toward “*design-for-recycling*” has emerged, focusing on polyolefin mimics such as aliphatic polyesters. Crucially, these strategies are complementary rather than mutually exclusive, as conventional chemical recycling methods can be readily repurposed to generate the telechelic macrodiols and diacids required to synthesize these chemically recyclable polyolefin analogues.

Recently, a growing number of literature reports has addressed the development of chemically recyclable polyolefin mimics. While a significant portion of these studies focuses on the synthetic protocols and basic characterization of these materials, the work presented in this thesis seeks to expand this scope. Specifically, this research aims to not only establish the structure-property relationships governing the performance of this polymer family but also to identify and validate their recycling pathways along with potential industrial applications.

Chapter II elucidates the synthesis and fundamental physicochemical properties of aliphatic long-chain polyethylene-like polyesters. Given that the selection of macromonomers often predefines the resulting thermomechanical performance, this chapter investigates the influence of monomer architecture and composition on the final polymer. Key findings will be presented on the synthesis, characterization, as well as mechanical and adhesive performance, of polyesters derived from both linear and branched polyethylene-based macromonomers.

In **Chapter III**, a dual recycling framework for these polyolefin-like polyesters is proposed and discussed. While the majority of current research focuses exclusively on the solvolysis of aliphatic polyesters followed by monomer recovery and repolymerization, this work broadens the circularity potential. A hybrid approach that includes both chemical deconstruction followed by repolymerization and the mechanical upcycling of these polymers through blend compatibilization strategies was investigated. Such dual approach aims to provide a more versatile solution for the management of mixed plastic waste streams. Finally, the utility of sustainable, potentially bio-based polyester^{127, 128}, poly(pentadecalactone)

(PPDL), was evaluated as a compatibilizer for mixed polyolefin blends comprising isotactic polypropylene (*i*PP) and high-density polyethylene (HDPE). Due to its long aliphatic methylene sequences, PPDL represents a promising polyethylene-like material closely mimicking the crystal structure, physical properties, and processing behavior of conventional polyolefins. Consequently, as indicated by its calculated solubility parameters¹²⁹, it exhibits likely affinity for both HDPE and PP despite the inherent immiscibility of the polyolefin pair.

In summary, this work aims to advance the field of chemically recyclable polyolefin-like polyesters by bridging material synthesis with practical performance evaluations and circular end-of-life strategies. Moving beyond basic material characterization, this research establishes fundamental structure-property relationships, detailing how macromonomer architecture dictates thermomechanical and adhesive performance. Furthermore, it demonstrates a hybrid recycling methodology, integrating chemical deconstruction with mechanical upcycling, to showcase that polyolefin-like materials can tackle current circularity limitations from two complementary angles.

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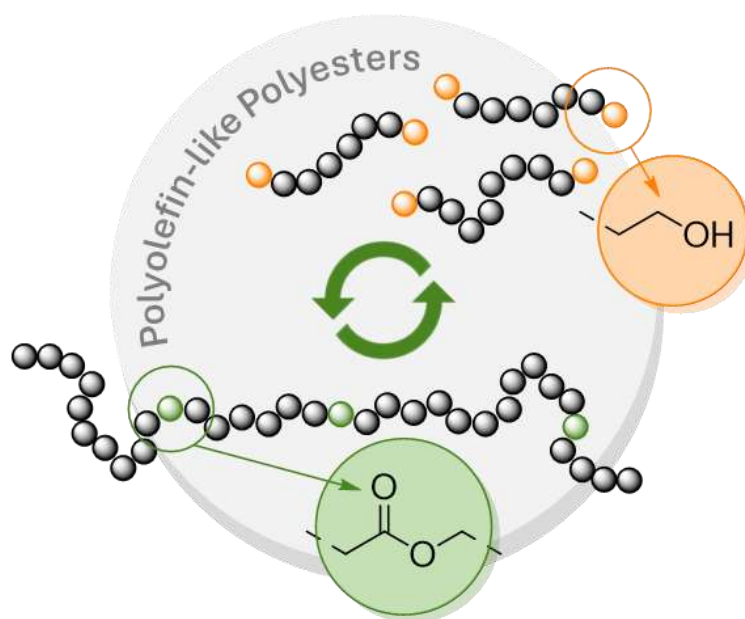
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CHAPTER II

Polyolefin-like Polyesters

This chapter elucidates the state of art in polyolefin-like polyesters, comprehensively reviewing their synthetic methodologies, structural characteristics, and material properties.



Publications included in this chapter:

1. Nowicka, W., Szot, W., Jasinska-Walc, L., Duchateau, R.; High-Molecular-Weight Polyesters Mimicking Linear Low-Density Polyethylene: Mechanistic Insight and Structure–Property Relationship; *ACS Applied Polymer Materials* **2025** 7(17), 12105-12116.
2. Nowicka, W., Rozanski, A., Pasha, F. A., Jasinska-Walc, L., Duchateau, R.; Polyethylene-like Polyesters: Strategies for Tailoring Mechanical Properties and Adhesion Performance; *Macromolecules* **2025** 58(17), 9440-9449

* The co-authors' approval to use this paper in the thesis was included with the documentation.

2. Introduction

The overview of polyolefin recycling pathways in the preceding chapter clearly underlines that a perfect solution has yet to be realized. Consequently, scientists, researchers, and engineers must continue to pursue strategies that simultaneously balance cost-effectiveness, scalability, environmental sustainability, and preservation of inherent material properties. As Mulhaupt concluded, the most efficient and environmentally friendly scenario for future plastic management must integrate multiple recycling methodologies to ensure both energy efficiency and complete material circularity.¹⁻³ One compelling strategy involves the structural redesign of these persistent, apolar macromolecules to introduce susceptibility to chemical recycling via mild solvolysis. To pursue this undeniably ambitious goal, a fundamental understanding of the thermomechanical and structural consequences of functionalizing the hydrocarbon backbone is crucial. In recent years, growing academic interest has focused on enhancing the circularity of polyolefins by inclusion of cleavable linkages within the polymer main chain. These functional groups can be selectively and easily broken to yield pristine monomers or low molecular weight oligomers suitable for subsequent repolymerization. Typically, carbon – carbon double bonds or heteroatom containing groups (N, O, S) are strategically incorporated, rendering the backbone prone to targeted catalytic deconstruction or nucleophilic attack during depolymerization. As the number of methylene repeating units between the polar ester groups increases, their disruptive impact on the bulk polymer properties diminishes.⁴ This dilution effect affords a much closer resemblance between conventional polyolefins and their circular analogues.

The concept of aliphatic long hydrocarbon chains with embedded ester functionalities can be traced back to 1930s and the groundbreaking work of Wallace Carothers on synthetic fibers.⁵ Carothers demonstrated that the inclusion of extended aliphatic segments promotes higher crystallinity, elevated melting temperatures (T_m), and stiffness. Inspired by these foundational principles, researchers have continued to develop and understand chemically recyclable polyolefin-like materials. A diverse array of synthetic strategies has been established, including the step-growth polymerization of long spaced α , ω -functionalized monomers^{6, 7}, the ring-opening polymerization (ROP) of macrolactones⁸, acyclic diene metathesis polymerization (ADMET)⁹, ring opening metathesis polymerization (ROMP)¹⁰, acceptorless dehydrogenative polymerization (ADP)¹¹, and coordination polymerization.¹² Among these numerous approaches, Mecking and co-workers have prominently popularized long-spaced

aliphatic polyesters derived from fatty-acid based renewable feedstocks.⁶ The recent surge in both academic and industrial interest in polyolefin-like architectures definitively demonstrates that materials mimicking the chemical structure and performance of polyolefins can be sustainably designed to enable end-of-life chemical circularity.

2.1 Synthetic pathways toward polyolefin-like materials

2.1.1 Step-growth polymerization

The origin of polyolefin-resembling polyesters traces back to Carothers who, as the research director for DuPont from the late 1920s through 1930s, employed classic organic chemistry reactions, specifically esterification and condensations, to construct novel architectures of macromolecules.⁵ His monumental discoveries, including nylon and neoprene, alongside his fundamental work on step-growth polymerization kinetics, built upon and ultimately validated Staudinger's macromolecular theory, laying the cornerstone of modern synthetic polymer science.¹³⁻¹⁵ In a paper published in 1932, he elucidated the synthesis of polyester-3,16, which he referred to as a "super-polyester" due to its distinctive mechanical robustness. Synthesized from hexadecanedioic acid (C_{16} -dicarboxylic acid) and 1,3-propanediol (C_3 -diol), this discovery pioneered the production of synthetic textile fibers, as these long-chain aliphatic polyesters enabled the drawing of fibers directly from the polymer melt.¹⁶ However, the melting point of these materials remained insufficient ($<110\text{ }^{\circ}\text{C}$) for widespread industrial application, while their high sensitivity to hydrolysis precluded their use in commercial textiles. Nonetheless, these fundamental efforts established the framework for high-performance, polyolefin-like polyesters possessing inherent degradability.

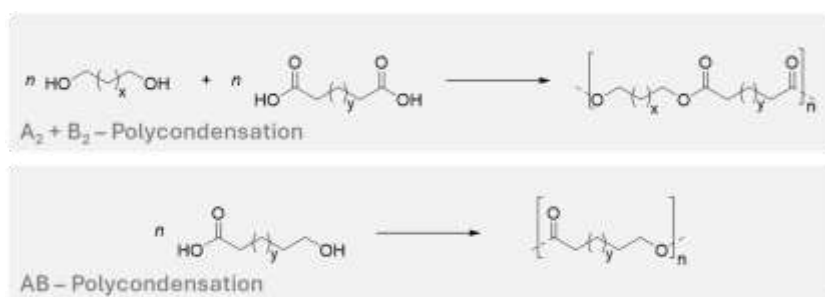
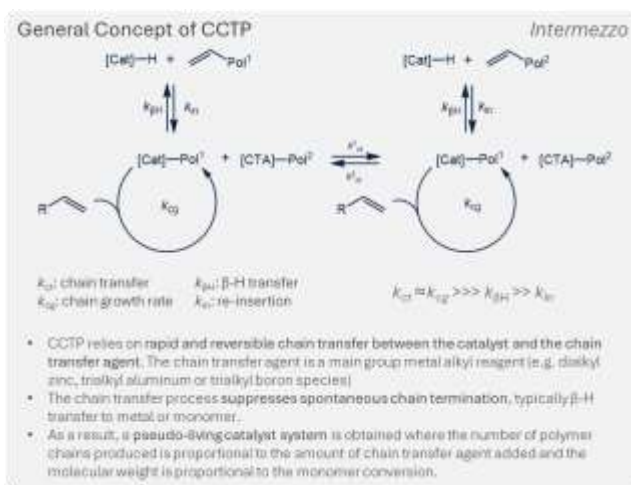


Figure 2.1. Schematic representation of step-growth polymerization of $A_2 + B_2$ polyesters from diacid and diol (top). Synthesis of AB-polyesters from hydroxy-acid bifunctional monomers (bottom).

The initial report explicitly classifying long-chain aliphatic polyesters as chemically recyclable polyolefin-like materials emerged from Shiono and co-workers. In their approach, the team performed a solution polycondensation of α , ω -dihydroxypolybutadiene with sebacoyl dichloride in the presence of pyridine, followed by a subsequent hydrogenation step. This pathway yielded materials exhibiting number-average molecular weights (M_n) ranging from 12 to 18 kg/mol with relatively broad polydispersities ($D_M = 4.5 - 7.1$). Furthermore, these polyesters offer complete chemical recyclability through hydrolysis, enabling monomer recovery.¹⁷ In concurrent study, Shiono investigated the synthesis of α , ω -bifunctional polyethylene-like polymers derived from *cis*-1,4-polybutadiene via metathesis reaction.¹⁸ This strategy was developed specifically with the objective of designing degradable polymers and preparing telechelic macromonomers optimized for the condensation of polyolefin-like polyesters.¹⁹ A similar approach was later employed by Long and co-workers to synthesize segmented polyethylene-based block copolymers via melt-polycondensation. Their strategy utilized two primary pathways: (i) the coupling of α , ω -dicarboxylic acid oligoethylenes with 1,6-hexanediol (or 1,6-hexanediamine)²⁰, or (ii) the reaction of α , ω -dihydroxypolyethylene with 1,2-octanediol and dimethyl succinate (Figure 2.1).²¹ Mechanistically, the polycondensation of AABB-type polyesters strictly demands precise stoichiometric equivalence between functional groups. Even minor imbalances, which are virtually inevitable when employing macromolecular precursors with molecular weight dispersity, severely limit the achievable degree of polymerization, yielding materials with compromised molecular weight characterized by mechanical brittleness. To circumvent the limitations of stoichiometric constraints, Tang introduced hydroxy-acid bifunctional telechelic oligoethylenes with varying 1-octene content (0 – 15 mol%) synthesized via coordinative chain transfer polymerization (CCTP) (for details see Intermezzo).¹² Because these precursors function as self-sufficient AB-type macromonomers, they undergo homopolycondensation into high-molecular weight polyethylene-like polyesters ($M_n = 27 - 46$ kg/mol) with predominantly narrow polydispersities ($D_M = 2.3 - 5.5$) without requiring a secondary comonomer (Figure 2.1).



Another elegant protocol wherein the stoichiometric balance during polycondensation does not restrict the final molecular weight of the resulting polyester was developed by Coates and co-workers to synthesize polypropylene-like architectures.²² In their approach, a copolymer of poly(propylene-*co*-butadiene) was first prepared via a hafnium-mediated catalytic process. The main chain unsaturations within the butadiene segments were subsequently used as selective cleavage sites during a cross-metathesis with 2-hydroxyethyl acrylate. Following quantitative hydrogenation, the resulting telechelic hydroxyethyl ester-functionalized macromonomers were subjected to melt-polycondensation, yielding circular polypropylene-like material with M_n of 33 kg/mol and slightly broader D_M of 4.5.

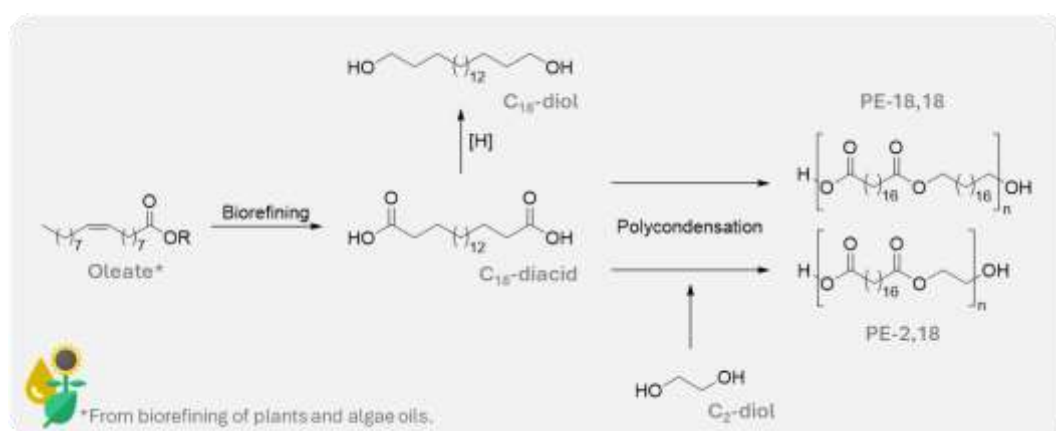


Figure 2.2. Synthesis of polyethylene-like polyesters PE-18,18 and PE-2,18 by polycondensation.²³

Mecking and co-workers are widely recognized as leading figures in the synthesis of recyclable long-spaced aliphatic polyesters (LSAPEs) that mimic polyolefins, utilizing long-chain building blocks derived from renewable feedstocks (Figure 2.2).^{4, 6, 7, 23-25} For instance, polyester-18,18 (PE-18,18) was synthesized from renewable 1,18-octadecanedioic acid, which was obtained via the olefin metathesis of biorefined plant oil feedstocks.⁷ Subsequent esterification and reduction of this dicarboxylic acid afforded the corresponding C_{18} dimethyl ester and C_{18} diol, which were utilized in a titanium (IV) butoxide-mediated $A_2 + B_2$ polycondensation. This catalytic protocol yields high-molecular-weight, HDPE-like polyesters, with number-average molecular weights (M_n) reaching up to 50 kg/mol and narrow dispersity ($D_M = 1.6$). The remarkably high molecular weight of PE-18,18 imparts robust rigidity and exceptional ductility, rendering these materials highly suitable for advanced processing techniques such as 3D printing and filament fabrication. Beyond polyethylene-like polyesters, the Mecking group has also pioneered

the catalytic synthesis of keto- and keto-ester-functionalized polyethylenes, systematically evaluating their susceptibility to photo-initiated degradation, as well as biodegradation.²⁶⁻³⁰

2.1.2 Ring opening polymerization (ROP)

Ring opening polymerization (ROP) of macrolactones, such as ϵ -decalactone, ω -dodecalactone, ω -pentadecalactone or ambrettolide, catalyzed by organometallic complexes^{8, 31-35}, organic molecules^{36, 37}, or enzymes³⁸⁻⁴⁰, yields linear, long-chain aliphatic AB-type polyesters. Within this class of materials, poly(pentadecalactone) (PPDL) has been extensively investigated by Duchateau and co-workers, primarily due to its striking structural similarity to polyethylene, which is reflected in alike thermal, crystalline and mechanical properties (Figure 2.3).^{8, 31, 33-36, 41-45} From a commercial standpoint, ω -pentadecalactone is a potentially bio-based macrocycle utilized within the fragrance industry as a musk component, though it can also be prepared via a 5-step synthetic protocol from petrochemical feedstocks.⁴⁶ Mechanistically, while the ring opening polymerization of small, strained lactones is an enthalpy-driven process fueled by the release of ring strain, the polymerization of macrolactones is inherently entropy-driven due to their negligible ring strain. Consequently, this entropic control and the prominence of transesterification and back biting reactions typically result in dispersity of 2.0 or higher.⁴² Nonetheless, the use of these macrolactones circumvents the generation of volatile condensates and eliminates the requirement for harsh high-vacuum, high-temperature operating conditions characteristic of traditional polycondensation strategies.

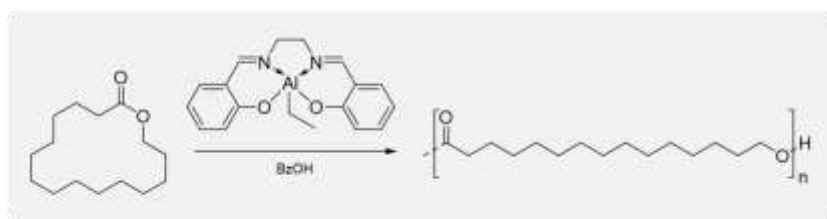


Figure 2.3. Ring-opening polymerization of pentadecalactone with an exemplary aluminum-salen complex.

The catalytic ring-opening polymerization (cROP) of ω -pentadecalactone utilizing economically viable aluminum-salen complexes yields polyethylene-like polyesters with number-average molecular weights reaching up to 155 kg/mol and narrow to moderate dispersities ($D_M = 2.0 - 2.8$).⁸ Although PPDL crystallizes within an orthorhombic unit cell identical to that of polyethylene, the presence of periodic in-chain ester moieties significantly suppresses the melting temperature (Figure 2.4). This thermal penalty stems from the forced

accommodation of the polar ester groups within the hydrocarbon crystal lattice, which lowers the overall enthalpy of fusion (ΔH_m). Consequently, despite demonstrating alike stiffness and mechanical properties, linear PPDL suffers from noticeably depressed T_m compared to HDPE (95 °C vs 130 °C, respectively).⁴¹ The structural similarity and thermodynamic affinity between these two polymers are further confirmed by crystallographic studies, which demonstrate the epitaxial crystallization of PPDL onto HDPE crystals, as evidenced by transmission electron microscopy (TEM).⁴⁵ A comprehensive elucidation of the influence of ester functionalities on the thermal and crystalline properties of polyolefin-like polyesters is provided in Subchapter 2.2.

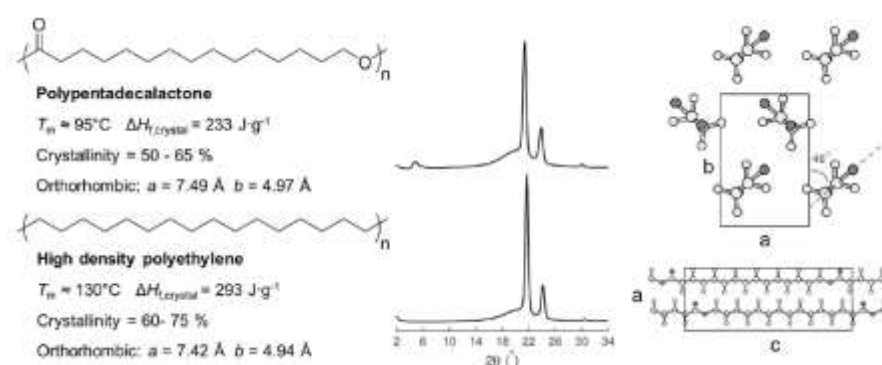


Figure 2.4. Comparison between the properties of PPDL and HDPE. Wide angle X-ray scattering patterns (WAXS) and corresponding orthorhombic unit cell of PPDL.⁴⁵

Beyond the linear architectures, PPDL can be modified to mimic branched polyolefins, such as LLDPE and LDPE. This is achieved by introducing short- and long-chain branching onto the unsaturated ambrettolide macrocycle via radical thiol-ene chemistry prior to polymerization.^{40, 44} In these branched architectures, an even more pronounced depression of T_m is observed as the bulky pendant alkyl branches are entirely excluded from the unit cell, disrupting crystalline packing far more severely. The synthetic simplicity of this approach, combined with the capacity to access both linear and branched topologies while maintaining tunable stiffness and high ductility (800 – 1000%)⁴⁴, underlines the great potential of macrolactone-derived materials.

2.1.3 Metathesis polymerization

In parallel to polycondensation and ring-opening polymerization, olefin metathesis, acyclic diene metathesis (ADMET) polymerization and ring-opening metathesis polymerization (ROMP), followed by hydrogenation, represent robust synthetic tools for the synthesis of polyolefin-like polyesters (Figure 2.5). ROMP is particularly powerful for the synthesis

of α,ω -dihydroxy-functionalized oligoethylenes, which serve as macromonomers in the step-growth polymerization of polyethylene-like polyesters. The main advantage of metathesis-based frameworks relies in their capacity to generate polymer chains with absolute structural precision, specifically driven by highly active ruthenium-based Grubbs and Hoveyda-Grubbs catalysts. Pioneering work by Wagener and co-workers elucidated ADMET polymerization of defectless precision polyolefins with periodically spaced cleavable groups from symmetrical α,ω -dienes containing an internal ester group.^{9, 47} To obtain fully saturated polyolefin mimics and exclude the effect of main chain unsaturations on polymer's characteristics, ADMET is followed by quantitative post-polymerization hydrogenation with heterogenous catalysts (eg. Pd/C) or homogenous alternatives (e.g. Wilkinson's catalyst $\text{RhCl}(\text{PPh}_3)_3$).⁴⁸

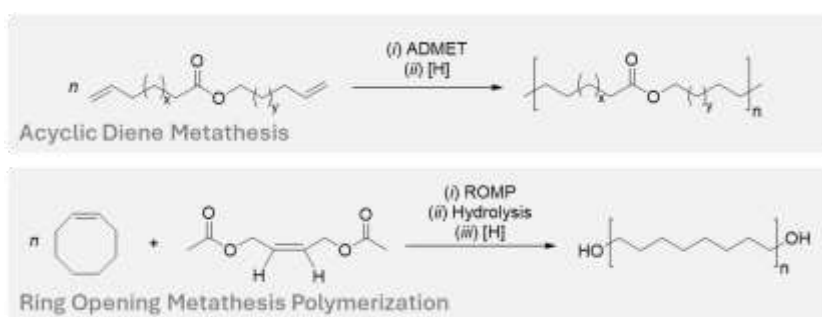


Figure 2.5. ADMET polymerization of α,ω -dienes containing an internal ester group. ROMP of *cis*-cyclooctene and *cis*-1,4-diacetoxy-2-butene yielding α,ω -dihydroxy oligoethylenes.

A straightforward and systematic approach for synthesizing high molecular weight, polyethylene-like polyesters with varying ester contents is the ROMP of ambrettolide and *cis*-cyclooctene.⁴¹ Subsequent exhaustive hydrogenation affords saturated polyesters ($M_n = 31 - 42$ kg/mol, $D_M = 2.2 - 3.4$) with methylene-to-ester ratios ranging from 15 to 229 and ∞ (mimicking pure polyethylene), displaying pseudorandomly distributed ester groups along the backbone. Physical characterization revealed that while these polymers maintain an orthorhombic unit cell and high crystallinity, their melting temperatures decrease proportionally from 132 °C to 91 °C with increasing ester content (for $M/E = \infty$ to $M/E = 15$).

An interesting approach for the synthesis of polyethylene-like polyesters was reported by Hillmyer and co-workers, wherein stoichiometrically self-balanced telechelic oligoethylenes ($M_n = 2 - 16$ kg/mol) yielded linear polymers via titanium (IV) butoxide-mediated polycondensation, achieving high molecular weights (M_n up to 111 kg/mol) with narrow dispersities (1.4 – 1.8).⁴⁹ A lack of regioselectivity during the metathesis chain-transfer step

with an unsymmetrical ambrettolide-derived CTA yielded a statistical mixture of chain-end combinations, specifically comprising ester-ester, ester-hydroxyl and hydroxyl-hydroxyl functionalities (Figure 2.6). Branched analogues of these materials were subsequently prepared utilizing a trifunctional chain extender, diethyl 5-(hydroxymethyl)isophthalate (DHIP). Due to the low fraction of ester groups embedded within the hydrocarbon backbones, the resulting polymers exhibited exceptionally high melting temperatures ranging from 131 °C to 135 °C. Consequently, their stress-strain profiles closely resembled those of pristine HDPE, demonstrating elongations at break up to 1200%. This striking performance and stoichiometric self-balance, combined with the inherent benefit of closed-loop recyclability, renders this a highly promising design.

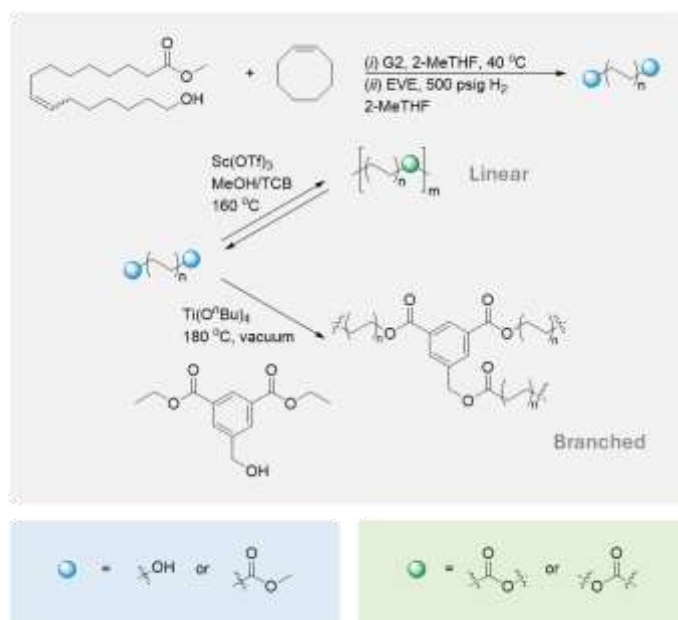


Figure 2.6. Synthesis of linear and branched polyethylene-like polyesters via ROMP of stoichiometrically self-balanced macromonomers.⁴⁹

In another work, Hillmyer elucidated ROMP of *cis*-cyclooctene and 3-hexyl-*cis*-cyclooctene with maleic anhydride as a chain transfer agent, followed by hydrogenation to synthesize carboxy-telechelic oligoethylenes.¹⁰ This approach afforded precise control over molecular weight, branching content, and resulting crystallinity. The resulting carboxy-telechelic oligoethylenes ($M_n = 5$ kg/mol) were subsequently crosslinked using bi- and trifunctional aziridines to yield chain extended elastomeric networks. This curing, driven by the reaction between carboxylic acid and aziridine functional groups, proved to be efficient, rapid, air-insensitive, and entirely byproduct-free. Owing to the step-growth nature of these chain

extension reactions, the cured polymers exhibited number-average molecular weights ranging from 20 – 50 kg/mol and dispersity ranging from 2.3 to 6.2.

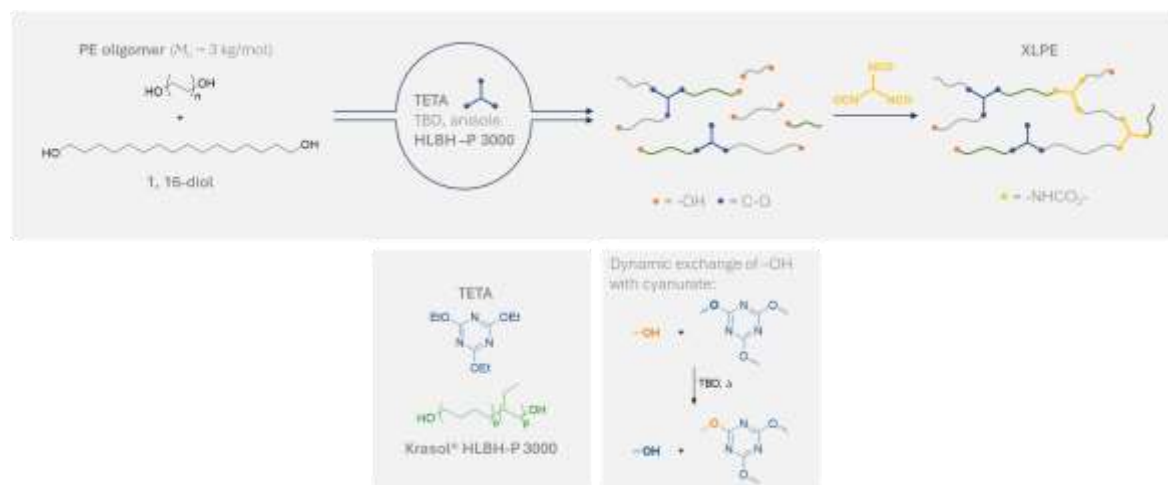


Figure 2.7. Synthesis of chemically recyclable cross-linked polyethylene.⁵⁰

A similar pathway for cross-linked polyethylene (XLPE) was developed by Miyake and co-workers (Figure 2.7).⁵⁰ In this approach, post-consumer LDPE and LLDPE were transformed into a chemically recyclable resin via a three-step protocol comprising: (i) dehydrogenation utilizing commercial hydrogen atom transfer (HAT) catalysts alongside transition metal catalysts, (ii) cross-metathesis of the unsaturated PE with *cis*-hexadec-6-ene-1,16-diol followed by hydrogenation, and (iii) the introduction of dynamic crosslinks via nucleophilic aromatic substitution (S_NAr) between the resulting PE-like diols ($M_n \sim 3$ kg/mol) and 2,4,6-triethoxy-1,3,5-triazine (TETA).⁵⁰ Finally, to endcap the remaining free hydroxyl moieties, a non-dynamic cross-linking agent, tris(6-isocyanatohexyl)isocyanurate (Tri-HDI), was introduced to yield a carbamate-linked thermoset. While Hillmyer's pathway employs purely structural chain extension, Miyake employed chemically recyclable dynamic covalent bonds. Nevertheless, both thermosets demonstrated similar mechanical and thermal profiles, characterized by excellent reprocessability, an absence of yield points, and elongations at break reaching up to 200%.

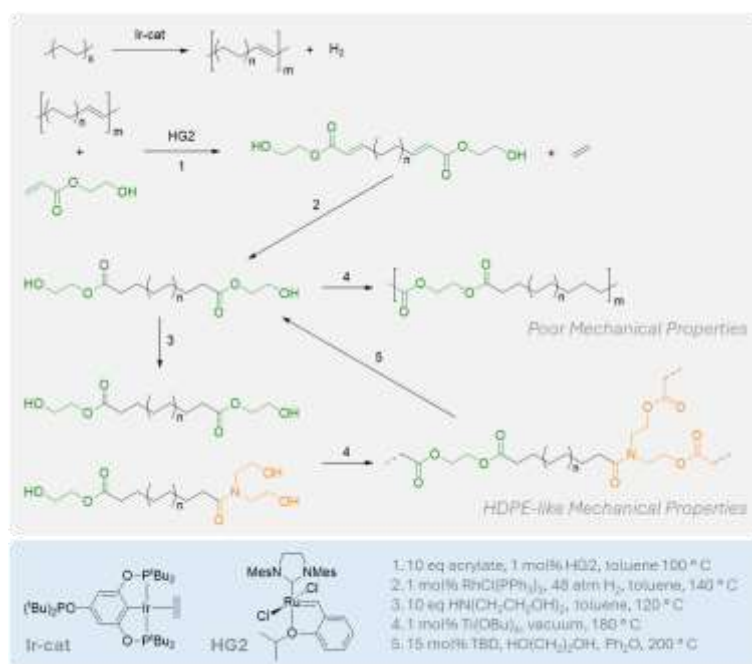


Figure 2.8. Transformation of post-consumer waste polyethylene into chemically recyclable polyethylene-like polymers.⁵¹

Another compelling route for the synthesis of polyethylene-like polyesters was demonstrated by Coates and co-workers, where post-consumer HDPE was employed as a chemical feedstock (Figure 2.8).⁵¹ Partial unsaturation was introduced into the HDPE backbone via acceptorless dehydrogenation catalyzed by an iridium-based pincer ethylene complex (Ir-POCOP).^{52, 53} A major advantage of this approach is its robustness, as it can be effectively applied to HDPE of varying molecular weights, dispersities, and impurity levels. The newly installed C=C double bonds were subsequently cross-metathesised with an excess of 2-hydroxyethyl acrylate in the presence of Hoveyda-Grubbs 2nd generation catalysts to introduce polar linking groups. The resulting chain-end unsaturations were then hydrogenated using Wilkinson's catalyst to yield a telechelic, PE-like macromonomer, which subsequently underwent polycondensation mediated by Ti(OBu)₄. While classical polycondensation initially yielded polyesters with poor mechanical properties ($M_w = 33$ kg/mol, $\epsilon_b < 5\%$), the introduction of a trifunctional cross-linker successfully overcame this limitation. The resulting ester- and amide-linked HDPE-like network exhibited a significantly higher M_w of 80 kg/mol, imparting excellent mechanical robustness with an elongation at break reaching nearly 1000%.

2.1.4 Acceptorless dehydrogenative polymerization (ADP)

In the field of step-growth polymerizations that circumvent strict monomer stoichiometry, Miyake and co-workers have emerged as leading pioneers in employing acceptorless dehydrogenative polymerization (ADP) to synthesize chemically recyclable, polyolefin-like materials with high precision.^{11, 54-59} ADP relies on the step-growth linking of unactivated alcohols or amines, bypassing the prerequisite of 1:1 functional group stoichiometry inherent to conventional polycondensation, to construct polyesters, polyamides, polyurethanes, and polyureas. Because molecular hydrogen (H_2) is liberated as the sole byproduct, monomer pre-activation is avoided, imparting fundamental atomic efficiency and end-of-life circularity to the process. Mechanistically, ADP represents a macromolecular adaptation of small-molecule acceptorless dehydrogenative coupling mediated by transition-metal catalysts (predominantly Ru-pincer^{54, 57-59}, Mn-complexes⁵⁵ and N-heterocyclic carbene (NHC) complexes⁶⁰) to sequentially dehydrogenate substrates without external redox reagents. The catalytic pathway comprises three principal steps: (i) coordination of an alcohol to the metal centre to form metal-alkoxide species that upon β -hydride elimination generates a carbonyl intermediate and metal hydride, (ii) nucleophilic attack of a second alcohol onto the generated carbonyl to form a hemiacetal intermediate, and (iii) subsequent dehydrogenation of the hemiacetal to regenerate the active catalyst and establish the ester linkage.¹¹

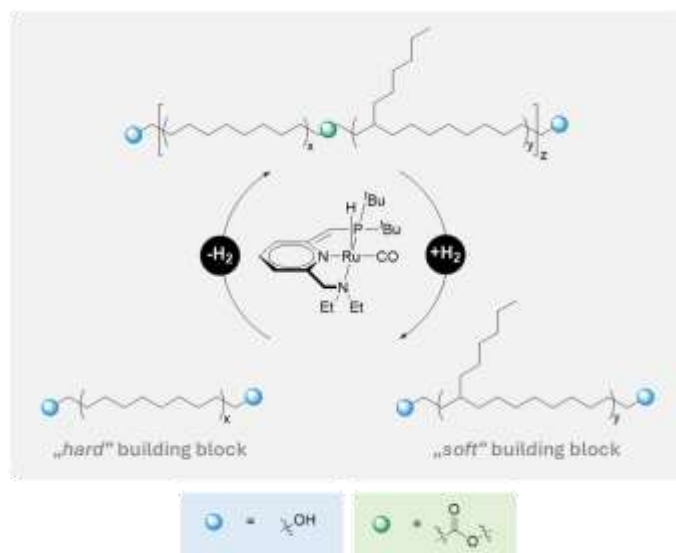


Figure 2.9. Polyolefin-like polyesters synthesized via acceptorless dehydrogenative polymerization.⁵³

Benefiting from this ADP platform to design structurally precise polyesters with structural circularity, Miyake and co-workers developed chemically recyclable, polyolefin-like multiblock

polyesters that effectively mimic the performance of OBCs. A series of high molecular weight multiblock polyesters ($M_w = 63 - 90$ kg/mol, $D_M = 2.2 - 2.7$) was obtained via a Ru-pincer catalyzed coupling of ROMP-derived macrodiols: a linear, crystalline “*hard*” block and a branched, amorphous “*soft*” block (Figure 2.9). The resulting materials exhibited elevated melting temperatures (106 – 124 °C), low glass transition temperatures ($T_g \approx -60$ °C), exceptional ductility (ϵ_b spanning 700 – 1000%) and significantly enhanced tensile toughness reaching up to 150 MJ·m⁻³.⁵⁴ Furthermore, the incorporation of polar ester groups along the hydrocarbon backbone provided an enhancement in adhesive strength to a variety of substrates, including aluminum, steel, PP and wood.^{58, 59} Closed-loop recycling of these materials was demonstrated via catalytic hydrogenolysis using the same Ru-pincer complex under 40 bar of H₂. Despite this unique balance of mechanical robustness and selective depolymerization, the current reliance on preparatory chromatographic column separation to isolate the initial hard and soft blocks presents a clear limitation to industrial scale. Consequently, discovering commercially viable, non-chromatographic separation methods for post-polymerization mixed macrodiols remains a critical point for future investigations.

2.2 Crystallization behaviors of polyolefin-like materials

2.2.1 The odd-even effect

Wide angle X-ray scattering (WAXS) of aliphatic long-chain polyesters (ALCPEs) reveals an orthorhombic unit cell characterized by prominent [110] and [200] reflections at $2\theta \approx 21.4^\circ$ and 24° , respectively, replicating the crystal lattice of conventional polyethylene.^{6, 23, 24, 61, 62} This crystal structure is dominated by the hydrocarbon segments, which arrange in an all-*trans* zig-zag conformation.⁶³ Remarkably, this polyethylene-like orthorhombic cell has been observed in polyesters with aliphatic spacings as short as PE-2,11.⁶⁴ Another hallmark characteristic of ALCPEs is the odd-even effect, which manifests as an alternating fluctuation of thermal properties, most notably the melting temperature, as a function of the number of methylene (CH₂) units between the ester linkages. In general, polyesters containing an even number of carbon atoms melt at higher temperatures than odd-numbered polyesters (Figure 2.10).

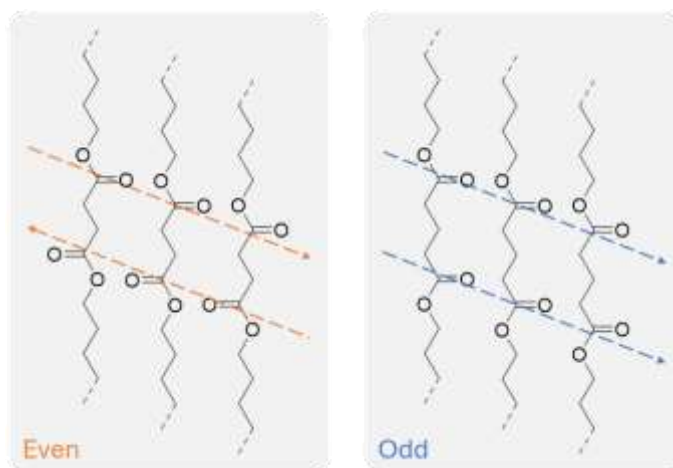


Figure 2.20. Schematic representation of the arrangement of ester units in aliphatic long-chain polyesters with even and odd numbers of carbons between ester groups. The direction of the dipole moments is indicated by arrows.⁶

Mechanistically, evenly spaced ester groups allow the polymer chain to form tightly packed crystalline layers where favorable dipole-dipole effects minimize steric frustration and maximize packing density within the crystal lattice. Conversely, odd-carbon spacers force ester groups into an asymmetrical orientation, disrupting the parallel dipole-dipole interactions and hindering optimal interchain packing. Consequently, odd-spaced ALCPEs exhibit systematically depressed melting points. As the length of the methylene spacers increases (typically exceeding 20 carbons), this effect fades, ultimately being dominated by the thermodynamic bulk properties of linear polyethylene ($T_{m(\text{HDPE})} \approx 135\text{ }^{\circ}\text{C}$).⁶

2.2.2 The Sanchez-Eby theory

Similarly to methyl and longer aliphatic branches, ester units can either reside in the amorphous phase or be accommodated within the crystalline fraction of polyethylene mimics. When incorporated into the crystal lattice, they act as localized structural defects along the polymer chains, imposing a thermal penalty (ε) that systematically decreases the melting temperature.⁴⁵ Under the inclusion hypothesis, a linear correlation is observed between T_m and the mole fraction of ester groups (X_E) (Figure 2.11). This thermodynamic behavior is described by the Sanchez-Eby equation⁶⁵:

$$T_m = T_m^0 \left(1 - \frac{\varepsilon}{\Delta H_m^0} X_E - \frac{2\sigma}{\Delta H_m^0 l} \right)$$

where T_m is the observed melting temperature of the aliphatic polyester, T_m^0 is the equilibrium melting temperature of the corresponding pristine homopolymer (e.g. HDPE), ε is the energy

penalty of the defect, ΔH_m^0 is the heat of fusion for linear polyethylene, X_E represents the mole fraction of integrated ester groups, σ and l denote the surface free energy of the crystal surface and the lamellar thickness, respectively.⁶

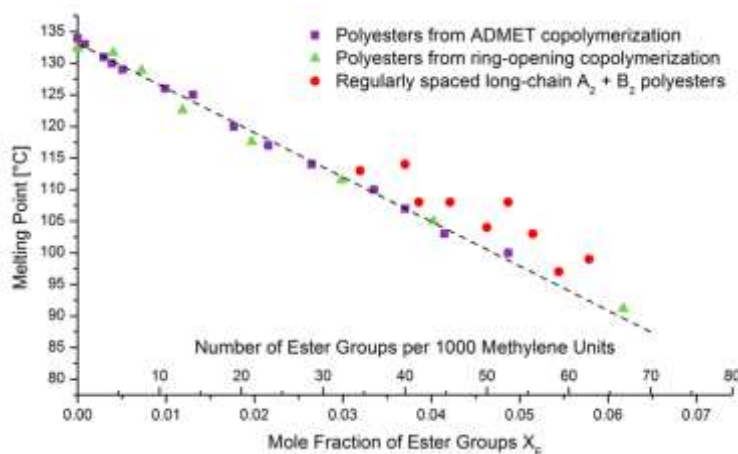


Figure 2.11. Melting points (T_m) of aliphatic long-spaced copolyesters from acyclic diene (■) and ring-opening metathesis copolymerizations (▲), as well as symmetrical, regularly spaced long-chain polyesters from $A_2 + B_2$ polyesterification (●) vs number of ester groups per 1000 methylene linkers and mole fraction X_E .^{6, 24, 41}

Consequently, the Sanchez-Eby theory provides a comprehensive physical model for correlating thermal transitions with localized structural distortions imposed by polar ester units or short-chain branching. Beyond influencing thermal properties, the inclusion of ester groups additionally results in diminished lamellar thickness of PE-like crystals in comparison with non-functionalized high-density polyethylene.⁶⁶ This subtle interplay between chemical structure, lamellar packing and thermal profiles is critical for the rational design of mechanically robust materials.

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2.3 High-Molecular Weight Polyesters Mimicking Linear Low-Density Polyethylene: Mechanistic Insight and Structure-Property Relationship

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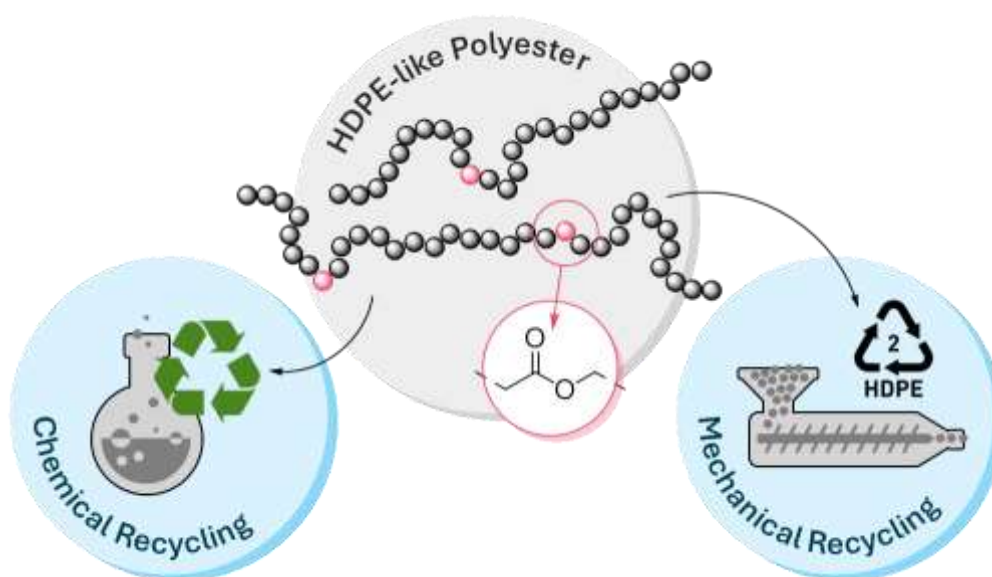
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IF₂₀₂₆ – 5.7; MNiSW – 140

CHAPTER III

Recycling of Polyolefin-like Polyesters

This chapter outlines the mechanical and chemical recycling pathways of polyethylene-like polyesters, underscoring their capacity to enable a closed-loop plastic economy.



Publications included in this chapter:

1. Nowicka, W., Szot, W., Rozanski, A., Yang, L., Gautam, P. S., Chinta, S., Verghese, N., Duchateau, R., Jasinska-Walc, L; Chemically Recyclable Polyester Miscible with HDPE Transforms Contamination into Functional Enhancement; *Macromolecules* **2026** 59(12), 6906–6913. Article selected for *Front Cover*.
2. Kruszynski, J., Nowicka, W., Rozanski, A., Liu, Y., Parisi, D., Yang, L., Pasha, F. A., Bouyahyi, M., Jasinska-Walc, L., Duchateau, R.; *i*PP/HDPE blends compatibilized by a polyester: An unconventional concept to valuable products; *Science Advances* **2024** 10(21), eado1944.

* The co-authors' approval to use this paper in the thesis was included with the documentation.

3. Introduction

This chapter outlines the circular economy of polyolefin mimics by exploring their dual chemical and mechanical recycling frameworks. Additionally, it will be demonstrated how polyolefin mimics can facilitate the recycling of polyolefin blends to restore their mechanical performance. The synthetic methodologies and macromolecular features of polyethylene-like polyesters detailed in the preceding chapter clearly demonstrate the robustness and structural versatility of these materials. A thorough understanding of the structure-property relationships governing their molecular, thermal, crystalline, and mechanical profiles reveals that polyethylene-like polyesters successfully match the performance criteria of numerous commercial-grade polyolefins across a diverse range of applications.¹

Yet, beyond these striking similarities, polyolefin-like materials must also undergo facile and quantitative depolymerization to fulfill the objectives of a closed-loop circular economy, a milestone currently unachieved by pristine polyolefins. This is accomplished through the incorporation of reactive in-chain polar functional groups (e.g., esters), which allow for the selective cleavage of the polymer chains.² Despite the presence of cleavable ester linkages, the highly apolar nature of the long hydrocarbon chains strongly impedes the biodegradation process. Consequently, the inherently limited environmental degradability of long-chain aliphatic polyolefin-like polyesters, and its implications as a mitigation strategy for conventional polyolefin accumulation, will be addressed in this section.

Given that commodity polyolefins are valued for their excellent melt-processability, polyolefin-like materials must similarly exhibit high thermal stability and resilience during mechanical reprocessing. As outlined in **Chapter I**, one of the primary limitations of mechanical recycling is the cross-contamination of mixed plastic waste streams, which compromises mechanical performance and causes a subsequent deterioration in the quality of the recyclates. One strategy for upcycling immiscible, and thus mechanically inferior, polyolefin blends is the use of compatibilizers—typically block or graft copolymers—which decrease dispersed phase droplet size and improve mechanical properties due to their enhanced affinity toward both phases. Polyolefin-like multiblock copolyesters offer a significantly more accessible and facile synthetic pathway in contrast to conventional olefin block copolymers. Because polyolefin-like materials not only structurally resemble pure polyolefins but are also fundamentally miscible and co-crystallizable with them (*vide infra*), along with synthetic advantages, there is tremendous potential in implementing them within

advanced recycling strategies.³ Given that polyolefins represent one of the highest volumes of plastic waste globally, these materials might be of particular interest as non-reactive macromolecular compatibilizers for mixed polyolefin streams. For instance, despite both being simple aliphatic hydrocarbons, HDPE and *i*PP are immiscible and exhibit pronounced phase separation upon mixing. Given that post-consumer polyolefin waste streams consist of 80 – 90% of either HDPE or *i*PP, combined with their commercial-scale production and technical limitations of sorting them, development of easily synthesizable compatibilizers is vital. Although numerous strategies for the compatibilization of polyolefin blends have been addressed in the literature, and are further elucidated in this chapter, the phase behavior and compatibility between polyolefin-like materials with pristine polyolefins remain, to the best of our knowledge, underexplored.

3.1 Polyolefin-like materials: Bridging the gap between polyolefins and polyesters

Among current plastic recycling strategies, mechanical recycling remains the preferred route due to its established infrastructure, lower energy demand, and reduced carbon footprint compared to chemical methods, making it the most promising method for achieving a circular plastics economy.⁴ This approach is widely applied to conventional polyolefins, polyesters and even blends thereof.⁵ The polyolefin-like polyesters demonstrate exceptional closed-loop recyclability over multiple cycles, driven by selective and clean cleavage of their labile ester linkages within their main chains. However, in real-world waste management scenarios, contamination of recycled streams is inevitable, which means that polyolefin mimics will eventually enter polyolefin recycling streams. Fortunately, due to the structural design of long-chain polyolefin-like polyesters engineered with long aliphatic sequences, they exhibit an intrinsic affinity for polyolefins. This miscibility prevents phase separation and, together with their alike crystalline and thermomechanical properties, ensures that the presence of polyolefin-like polyesters is unlikely to compromise the quality of the recyclate. Thus, it is crucial to estimate the compositional range of blends maintaining miscibility and preserving the desired mechanical performance, as explained later in this section.

When mechanical recycling reaches its limits, typically after multiple reprocessing cycles that unavoidably degrade polymer integrity, chemical recycling gains momentum due to its ability to recover pure monomers or oligomers. Conventional polyolefins, comprising strictly inert C–C backbones, cannot be selectively depolymerized into their monomers under mild conditions. Consequently, their chemical recycling relies on energy-intensive strategies, such as pyrolysis or gasification, which often yield complex product mixtures that require further purification (see Section 1.3.3 for details). In contrast, polyolefin-like polyesters occupy a unique middle ground between standard polyolefins and polyesters, such as poly(ethylene terephthalate) (PET), poly(lactic acid) (PLA), polycaprolactone (PCL), and poly(butylene succinate) (PBS). In terms of their solid-state performance, polyolefin-like polyesters retain high mechanical strength, elevated crystallinity and thermal properties characteristic of polyethylene. Chemically, however, the incorporation of ester linkages grants them with polyester-like reactivity, enabling selective depolymerization via alcoholysis. Under mild solvolytic conditions, these polyolefin-like polyesters undergo complete chemical depolymerization to yield their starting monomers in high purity (> 90%). Crucially, since pristine polyolefins remain entirely unreactive under

these conditions, this chemical reactivity provides an efficient, closed-loop route to selectively isolate and recycle polyolefin-like materials directly out of mixed waste streams in the form of pure macromonomers.^{6,7}

3.2 Mechanical recycling of polyolefin-like materials

Polyethylene-like polyesters, including PE-19,19, PE-23,23, and PE-18,18, can be readily processed using standard techniques common across the plastics and recycling industries, such as melt compounding, injection molding, film extrusion, and fiber spinning.⁸ Notably, PE-18,18 and the polycarbonate PC-18 have been successfully utilized in fused filament fabrication (FFF) for 3D printing applications.⁷ Furthermore, due to its facile processability, PE-2,18 can be melt spun into synthetic fibers tailored for textile applications, offering the added benefit of biodegradability.⁹ Collectively, these processing capabilities demonstrate that polyethylene-like materials exhibit susceptibility to conventional mechanical recycling as that of commodity polyolefins. Moreover, given the structural similarity of these materials to their pristine polyolefin counterparts, their scope of application can be further extended by blending them with compatible polymers or employing them as macromolecular compatibilizers.¹⁰

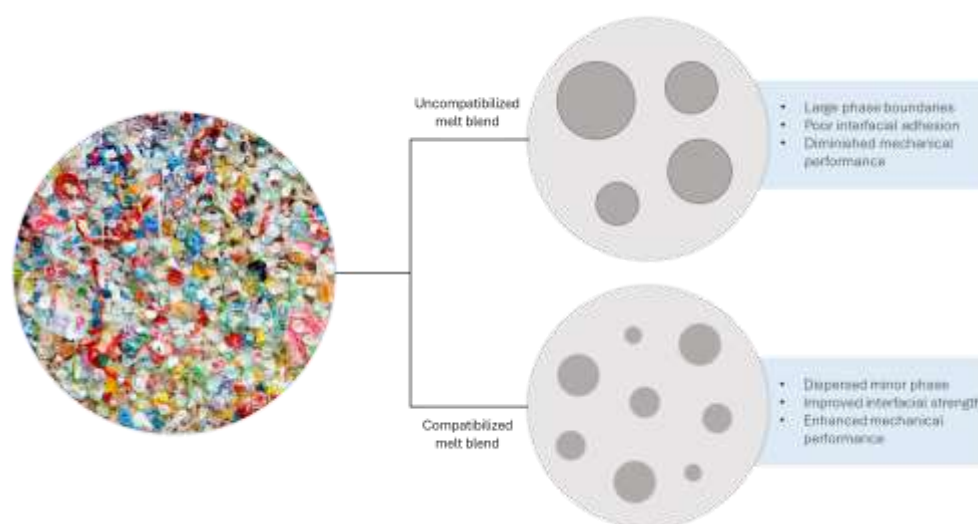


Figure 3.1. Schematic representation of compatibilization of immiscible polymer blends with a nonreactive compatibilizer.

The term compatibilization refers to the introduction of a macromolecular additive that effectively increases the interfacial adhesion between the components of an immiscible polymer blend, thereby transforming its morphology (Figure 3.1). In particular, multiblock,

graft and comb architectures of PP- and PE-based copolymers, along with polyolefin elastomers such as EPR, EPDM, LLDPE and OBCs, serve as effective compatibilizers for PP/HDPE blends.³ At a molecular level, these dual-affinity copolymers exhibit compatibility with both *i*PP and PE phases, a property further governed by branching content. For example, during compatibilization with LLDPE, increased comonomer incorporation introduces higher branching density (diminished crystallinity), thereby enhancing miscibility with the polypropylene phase.¹¹ While an uncompatibilized blend typically exhibits poor mechanical performance due to macro-phase separation with large, coarse domains, successful compatibilization yields a fine dispersion of the minor phase within the continuous matrix, ultimately enhancing the bulk mechanical properties.¹² There are numerous mechanisms leading to this morphological refinement, such as co-crystallization between components, entanglements, tie molecules or formation of micelles.³ Co-crystallization, defined as the incorporation of the compatibilizer into at least one, and preferably both, of the blend's phases, is essential for preserving the high modulus and stiffness of *i*PP while maintaining the facile processability of PE. Naturally, interfacial co-crystallization is influenced by multiple interrelated factors, including processing conditions, melt viscosity, blend composition, component microstructures, and relative crystallization rates. Because crystallinity alone may not be sufficient to prevent interfacial failure via chain pull-out, molecular entanglements play a critical role in reinforcing the interfacial boundary. Similarly, tie molecules mitigate premature failure by bridging crystalline lamellae across amorphous regions, thereby enhancing overall blend toughness.¹³ Ultimately, because reinforcement occurs within both bulk phases and at the interface, optimizing these structural parameters enables the restoration of mechanical performance even at relatively low compatibilizer loadings.

3.2.1 Miscibility of polymer blends

Given that the application of polyethylene-like materials as macromolecular blend components and compatibilizers represents the primary focus of the investigations presented in this chapter, establishing the theoretical foundations of polymer miscibility is vital. Generally, binary polymer blends are classified into three categories: (i) fully miscible, (ii) partially miscible, and (iii) immiscible systems.^{14, 15} Fully miscible blends form a homogeneous phase on a molecular scale across the entire composition and temperature range, as exemplified by the polystyrene/poly(phenylene oxide) system.¹⁴ When dealing with semicrystalline components, miscibility may manifest as co-crystallization. This phenomenon typically requires highly matching chain conformations, chemical compatibility, and analogous crystal

lattices, as observed for closely related HDPE and LLDPE blends at specific compositions.¹⁶ Conversely, if the energetic penalty for accommodating both components within the same crystal lattice is exceedingly high, independent crystallization of the respective homopolymers occurs due to crystallization-induced phase separation. Consequently, the ultimate morphology and crystalline structure of miscible blends are strongly governed by composition, the chemical architecture of the individual components, and the prevailing thermal history. Partially miscible blends exhibit a narrower window of compatibility strictly dictated by specific composition and temperature regimes, transitioning to a phase-separated morphology outside of these boundaries. Lastly, a complete lack of thermodynamic affinity and mutual insolubility results in the phase-separated morphologies characteristic of immiscible polymer blends, a scenario that describes most synthetic polymer pairs.

The phase behavior of polymer blends is fundamentally described by the Flory-Huggins theory, a thermodynamic model that accounts for the significant discrepancies in molecular size between polymers and small molecules by defining the entropy of mixing.^{17, 18} To determine whether spontaneous mixing occurs, which requires the Gibbs free energy of mixing (ΔG_m) to be negative, the free energy change per mole is applied:

$$\Delta G_m = RT \left[\frac{\phi_A}{x_A} \ln \phi_A + \frac{\phi_B}{x_B} \ln \phi_B + \chi_{AB} \phi_A \phi_B \right]$$

where R is the ideal gas constant, T is the absolute temperature, $\phi_{A/B}$ denote the volume fractions of component A and B in the blend, respectively, and $x_{A/B}$ represent their number of segments in polymer chain. The χ_{AB} is the Flory-Huggins interaction parameter (χ). The first two terms of this expression represent the entropic contribution to mixing. Due to the macromolecular size of polymer chains these terms become small, indicating that polymers possess negligible entropy-driven force for blending. While the last term comprising interaction parameter refers to enthalpic contribution. To reach the scenario where the polymers exhibit mutual attraction and facilitate mixing, the interaction parameter must typically be negative ($\chi_{AB} < 0$). Since χ parameter is temperature-dependent, altering the temperature significantly shifts the thermodynamic balance, directly governing the phase behavior and overall stability of the polymer blends.¹⁷

3.2.2 Miscibility between polyolefins and polyolefin-like materials

An elegant predictive approach based on group contribution theory for assessing the thermodynamic miscibility of binary polymer blends was established by Hoftyzer and van Krevelen, who utilized the contributions of individual structural groups to determine

the solubility parameters of polymers via the calculation of total cohesive energy.¹⁸ Typically, close agreement between solubility parameters indicates enhanced compatibility or potential miscibility between blend components. Theoretical evaluation of the miscibility between the polyolefin-mimicking poly(pentadecalactone) (PPDL) and HDPE yielded calculated solubility parameters of $17.21 \text{ J}^{1/2} \cdot \text{cm}^{-3/2}$ and $16.13 \text{ J}^{1/2} \cdot \text{cm}^{-3/2}$, respectively (see paragraph 2.1.2).¹⁵ Interestingly, *i*PP exhibited a solubility parameter ($17.12 \text{ J}^{1/2} \cdot \text{cm}^{-3/2}$) remarkably close to that of PPDL.¹⁵ For instance, metallocene-based HDPE and PP exhibit enhanced interfacial affinity through molten-state chain entanglements that lock in place upon crystallization, whereas Ziegler-Natta polymers lack adhesion owing to low molecular weight amorphous fractions at the interface.¹⁹ However, given that majority of HDPE and *i*PP pairs is inherently immiscible, a similar phase-separation trend was anticipated for the PPDL/PP pair. Consequently, this unexpected parameter proximity served as the inspiration for further investigation into ternary PP/HDPE/PPDL blends (vide infra, see Subchapter 3.6).

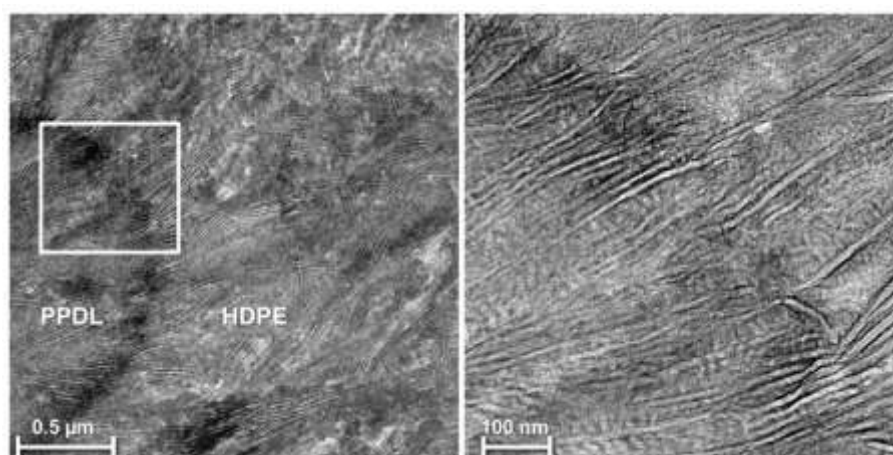


Figure 3.2. TEM morphology of a PPDL/HDPE 10/90 wt% composition. White square indicates enlarged area with the interfacial region presented on the right handsight of the figure.^{15, 20}

Experimental validation of binary PPDL/HDPE systems prepared via melt extrusion revealed the development of a phase-separated morphology at the onset of crystallization. However, the exceptional compatibility of this system is clearly evidenced in transmission electron microscopy (TEM) micrographs of the interfacial region in the 10/90 wt% PPDL/HDPE blend, where numerous lamellae penetrate through the PPDL–HDPE phase boundary, displaying clear epitaxial growth of PPDL lamellae onto the HDPE substrate (Figure 3.2).²⁰ Remarkably, crystal growth proceeds in an uninterrupted manner across the interfacial boundary of this two-phase system owing to the low interfacial energy between the components. As a result, the interfacial PPDL crystals adopt the same unit cell dimensions and lamellar thickness as the matrix HDPE. Similarly, blends of PPDL and LDPE investigated

across a wide compositional range (10 - 90 wt%) exhibited phase separation at the onset of crystallization.²⁰ In PPDL-rich formulations, a characteristic shish-kebab morphology was observed, which was presumably induced by flow-induced crystallization during the extrusion process. Conversely, LDPE-rich compositions demonstrated prominent epitaxial crystallization, adapting their lamellar thickness and domain orientation in a manner analogous to that observed in the PPDL/HDPE blends. These highly integrated interfaces with shish-kebab structures minimize stress concentrations during deformation, which ultimately translates into enhanced mechanical performance and exceptionally high elongation at break, driven by the epitaxial co-crystallization at the phase boundary. In summary, although HDPE, LDPE, and PPDL are classified as mutually immiscible by conventional criteria, their highly similar solubility parameters and matching unit cell dimensions promote enhanced interfacial adhesion, ultimately yielding mechanically robust interphases.

3.3 Chemical recycling of polyolefin-like materials

3.3.1 Solvolysis

Chemical recycling via solvolysis to monomers or oligomeric intermediates emerged as a promising solution to the inherent limitations of conventional mechanical recycling.^{21, 22} Polyethylene-like polyesters are of particular interest because they can undergo chemical depolymerization in a manner similar to PET, which is industrially recycled back to for example terephthalic acid, dimethyl terephthalate monomers, or oligomeric intermediates.²³ Taking advantage of this concept, Mecking and co-workers have repeatedly demonstrated that polyethylene-like materials synthesized via polycondensation can be efficiently recycled under mild conditions via alcoholysis.^{1, 7, 10, 24, 25} For instance, the polyesters PE-2,18 and PE-18,18, alongside the polycarbonate PC-18, depolymerize completely in a basic ethanol solution (10 wt% KOH) at 120 °C, or alternatively in methanol at 150 °C, yielding monomer recoveries of up to 98 mol%.⁷ The addition of KOH as a catalyst accelerates this reaction, enabling reaction completion within a few hours at temperatures between 120 °C to 180 °C. Due to the facile crystallization of the long chain aliphatic monomers (C₁₈ dimethyl ester and diol), they can be readily recovered from the homogenous post-reaction mixture via crystallization or solvent evaporation.^{7, 26} Chemical recycling of PE-18,18 yields a non-separable monomeric mixture due to the low volatility of both the C₁₈ dimethyl ester and the C₁₈ diol. Nevertheless, the high purity of recovered monomers and their preserved 1:1

stoichiometry enable direct, subsequent repolymerization, ultimately achieving a 96% polymer-to-polymer recovery.⁷ Conversely, when subjecting polymers containing long crystallizable segments and small, volatile linkers (e.g. diethylcarbonate, ethylene glycol) to alcoholysis, physical separation of the components is feasible. This closed-loop recycling strategy has also proven effective for polyesters comprising multiple chain length building blocks ($C_4 - C_{20}$ dicarboxylic acid monomers).²⁵ Furthermore, the selective depolymerization of PE-18,18 and PC-18 has been validated in recycling of model waste streams. High-purity monomers were recovered while conventional polyolefins, colorants and PET remained completely unaffected.⁷

Although long-chain aliphatic polyesters can be chemically recycled at elevated temperatures via alcoholysis, acid- or base-promoted depolymerization, they remain remarkably persistent under ambient environmental conditions. To enhance the predisposition toward hydrolytic degradation, as exemplified by PE-18,18, a minor fraction of hydrolytically responsive poly(H-phosphonate) (PHP) was incorporated into the matrix.²⁷ This modification not only results in the hydrolysis of the phosphonate component itself but also accelerates the degradation of the surrounding polyethylene-like matrix via the in situ generation of PHP-derived phosphoric acid. Alternatively, the incorporation of small quantities of sulfonic acid groups within the polyethylene-like main chain promotes acid-catalyzed hydrolysis while simultaneously imparting the benefit of enhanced surface printability.²⁸

3.3.2 Catalytical hydrogenation

An elegant alternative approach toward closed-loop recyclable polyethylene-like polyesters was demonstrated by Miyake and co-workers, who employed the acceptorless dehydrogenative polymerization of linear and branched diols.^{6, 29-34} Notably, the exact same catalytic system, typically comprising iridium⁶ or manganese complexes²⁹, can be employed in reverse for the depolymerization of these polyesters via catalytic hydrogenation back to the diol monomers. The monomer recovery yield depends heavily on the chemical structure: branched, amorphous diols require purification via preparative column chromatography, limiting their overall isolated yield to 92 %, whereas linear, crystallizable diols can be recovered in up to 98 % yield.⁶ This closed-loop strategy ensures exceptional property retention, with the recycled polymers exhibiting thermal and mechanical profiles virtually identical to those of their pristine counterparts. Furthermore, in line with Mecking's findings, this catalytic hydrogenation protocol proved highly selective, successfully depolymerizing the target polyesters within

mixed-waste streams containing commodity polymers such as HDPE, LDPE, PP, and nylon-6,6.²⁹

3.4 Can polyolefin-like materials be biodegradable?

While the systemic leakage of plastics into the natural environment, often elicited by inefficient collection systems, remains a critical issue, its negative impact can be mitigated by the biodegradability of alternative polymers. Susceptibility to biodegradation is governed by the interdependent nature of multiple factors, including molecular weight, chemical structure, and macromolecular morphology.³⁵⁻³⁷ Crucially, the presence of hydrolyzable polar functional groups (e.g. esters, amides) along the polymer backbone is a prerequisite for facile degradation. Regarding morphology, highly crystalline and semicrystalline polymers are inherently less prone to biodegradation, as enzymes typically penetrate and attack target bonds located exclusively within the amorphous phase.³⁵ Recent studies have demonstrated that the majority of isolated carbonyl groups within semicrystalline, polyethylene-like materials, are located primarily at the crystalline-amorphous interface.^{38, 39} Mechanistically, polymer biodegradation is initiated via chain scission into low-molecular-weight intermediates, which are subsequently mineralized by microorganisms (such as bacteria, fungi, and algae) into CO₂, O₂, and biomass, or CH₄ under anaerobic conditions.¹⁰ Industrial composting under optimized parameters, such as controlled moisture, temperature, pH, and oxygen levels, proceeds at an accelerated rate compared to slow, abiotic hydrolytic degradation in natural ecosystems. Thus, environmental conditions substantially control degradation kinetics and efficiency.

The primary representatives of synthetic biodegradable polymers are short-spaced aliphatic polyesters, such as poly(lactic acid) (PLA), poly(glycolic acid) (PGA), polycaprolactone (PCL), and poly(butylene succinate) (PBS).³⁵ However, the biodegradability of long-spaced aliphatic polyesters differs significantly, as demonstrated by Heise and co-workers using the macrolactone-based polyester PE-15.⁴⁰ Even after incubation in a phosphate-buffered solution at 37 °C for two years, and upon the subsequent addition of enzymes, the samples exhibited remarkable hydrolytic stability with no observable mass loss or changes in crystallinity. Similarly, Mecking's long-chain polyester PE-18,18 showed no degradability in acidic or basic solutions, confirming that long-spaced aliphatic polyesters are too crystalline and hydrophobic to undergo degradation even under harsh conditions.⁴¹

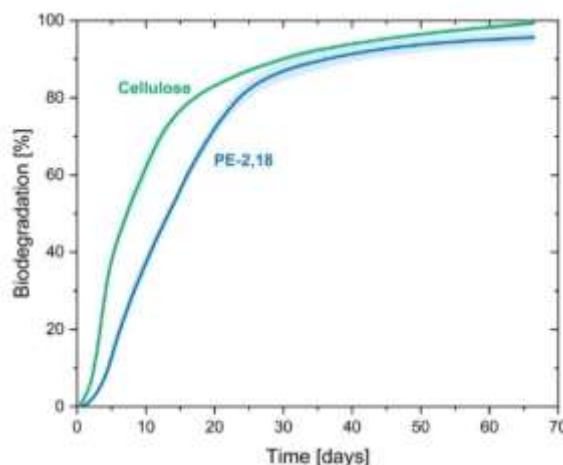


Figure 3.3. Mineralization curves based on carbon dioxide evolution evaluated under industrial composting conditions for PE-2,18 and cellulose reference (ISO 14855-1, 2 months at 58 °C).³⁷

Interestingly, systematic assessment of polyesters synthesized from 1,4-butanediol and C_4 to C_{18} dicarboxylic acids (PE-4,4 to PE-4,18) evidenced that, regardless of chain length, all such polyesters undergo enzymatic hydrolysis and industrial biodegradation, achieving mineralization levels exceeding 95 % within two months.⁴² Likewise, segmented polyesters comprising mixed-chain-length blocks (ethylene glycol combined with $C_4 - C_{20}$ dicarboxylic acid monomers) undergo mineralization under much milder conditions in agricultural soil, highlighting their potential to degrade if released into the natural environment.²⁵ Remarkably, the mineralization profile of the semicrystalline polyester PE-2,18 closely mirrors the degradation behavior of commercial cellulose (Figure 3.3).³⁷ Mechanistic research has demonstrated that long-chain diol segments lead to significantly lower depolymerization rates compared to shorter diols. For instance, the hydrolysis of PE-4,18 is roughly 20 times faster relative to PE-18,4.⁴³ It has been proposed that the highly hydrophobic long-chain diol monomer, once cleaved during initial degradation, remains within the bulk polymer, effectively shielding the remaining intact ester bonds from enzymatic attack and hampering further hydrolysis.

Conventional polyolefins resist biodegradation under both industrial composting and standard environmental conditions due to their inert, non-polar backbones and absence of reactive functional groups. A similar trend applies to the polyolefin-like polyesters investigated in this work. The incorporation of ultra-long aliphatic segments, comprising at least 100 carbons in the main chain, imparts a dominant apolarity to the polymer chains. Consequently, this high hydrocarbon character effectively limits enzymatic recognition, thereby precluding biodegradation.

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3.5 Chemically Recyclable Polyester Miscible with HDPE Transforms Contamination into Functional Enhancement

This subchapter has been published as:

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IF₂₀₂₆ – 5.7; MNiSW – 140

3.6 iPP/HDPE Blends Compatibilized by a Polyester: An Unconventional Concept to Valuable Products

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DOI: 10.1126/sciadv.ado1944

IF₂₀₂₆ – 13.9; MNiSW – 200

Summary

Polyolefins, with polyethylene and polypropylene remaining the most widely produced in global scale, are undeniably crucial for contemporary society, having permeated nearly every aspect of daily life – from healthcare, construction, and packaging to electronics and automotive applications. The combination of cost-effectiveness, lightweight nature, facile processability, and mechanical integrity renders them virtually irreplaceable in the majority of applications. Yet, their environmental persistence, along with growing concerns regarding plastic waste mismanagement, calls for more sustainable solutions that offer high performance alongside a circular end-of-life strategy – such as susceptibility to solvolysis, typically achieved by incorporating labile polar groups. This thesis focuses on exploring the potential and limitations of chemically recyclable polyolefin mimics, with an emphasis on polyethylene-like polyesters and a thorough understanding of their: (i) polymer topology, (ii) chemical composition and its influence on structure–property relationships, (iii) application-oriented characterization, and (iv) ability to mimic conventional polyolefins, also in the applications like hot melt adhesives, as closely as possible while remaining fully circular.

The first scientific paper presented in this thesis investigates the ring-opening metathesis polymerization of *cis*-cyclooctene with 3-hexyl-*cis*-cyclooctene to synthesize branched polyethylene-like macrodiols. Subsequent polycondensation of a selected macrodiol with an excess of succinic anhydride yielded a high-molecular-weight LLDPE-like polyester with thermomechanical properties matching those of commercial materials, alongside the high added value of enhanced adhesion. A similar protocol was subsequently used to prepare a family of polyethylene-like polyesters from just two building blocks – crystalline and amorphous dihydroxy-telechelic oligoethylenes. The ability of succinate end groups to undergo backbiting and subsequently release succinic anhydride units proved efficient in securing the correct reaction stoichiometry, thereby yielding high-molecular-weight products. In addition, it was demonstrated that a succinate unit introduces a crystal lattice defect similar to that of a single ester group, allowing high melting temperatures to be preserved. An inverse correlation between branching content and crystallinity, alongside the absence of such a correlation between branching content and melting temperature, highlighted a characteristic feature of multiblock copolymers, where the melting point is dictated solely by the hard block content. Concurrently, by adjusting the ratio between soft

and hard macrodiols, the viscoelastic properties, mechanical performance, and adhesion to polar substrates like aluminum can be finely tuned. Molecular dynamics simulations highlighted the significant role of the branched, amorphous block in governing adhesion, as increasing the soft block content significantly disrupts lamellar packing, hampering uniform surface wetting and thereby decreasing the density of polar groups at the bonding interface.

Recycling strategies for polyethylene-like polyesters were investigated within a dual framework, wherein they can either be depolymerized via alcoholysis or blended into polyolefin matrices. A study of the miscibility between HDPE and HDPE-like polymers demonstrated that they are completely miscible, forming cocrystallized single-phase systems across all compositions. Consequently, the HDPE-like polyester can be processed alongside commercial polyolefins without creating a distinct waste stream, thereby removing the requirement for specialized sorting. This compatibility enables dual-pathway recycling: direct mechanical reprocessing of blended waste streams or selective methanolysis of the HDPE-like component back to pristine monomers. Remarkably, incorporating as little as 20 wt% HDPE-like boosts adhesion to aluminum over ten-fold while retaining exceptional ductility, a performance gain that persists even in heterogeneous post-consumer recycled HDPE. Ultimately, this work proves that chemically recyclable polyesters can easily integrate with commodity polyolefins, upgrading low-value waste streams rather than degrading them.

Another polyolefin-like material evaluated in this work is poly(pentadecalactone) (PPDL), a long-chain aliphatic polyester with 14 methylene units per ester group. Due to its highly similar crystalline structure, PPDL closely mimics the properties and mechanical performance of HDPE. The use of PPDL as a compatibilizer for immiscible *i*PP/HDPE blends proved to be a highly effective strategy, transforming brittle compositions into exceptionally tough materials that even outperform pristine *i*PP and HDPE. This astonishing effect of PPDL is dual in nature, as it grows epitaxially from HDPE crystals and mixes into the amorphous *i*PP phase, as evidenced by TEM and molecular dynamics simulations. This affinity for both phases provides interfacial reinforcement while significantly reducing the dispersed phase domain size from 400 nm to 200 nm, consecutively. In contrast to complex multiblock or graft PP–PE copolymer architectures, this approach achieves mechanical integrity utilizing a single, simple polyester. Owing to its inherent simplicity, this strategy is readily scalable and offers immense potential for transforming large volumes of polyolefin waste into high-value products.

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During the final days of my Master's internship, when I already knew I would continue with a PhD, Rob told me, "*Be aware that these years will be the best ones of your career and at the same time extremely challenging.*" And they truly were. It was a beautiful journey filled with the kindest, most caring people, constant support, endless coffees, even more laughter, comfort in difficult times, and celebration in good ones. This entire experience helped me grow not only as a researcher, but also as a person. I discovered new horizons and pushed boundaries I didn't even know existed. I could easily turn these acknowledgments into a catalogue of professional glorification, but all of that is already documented in this thesis, which is why I decided to take a different approach.

First, I would like to express my deepest gratitude to Prof. DSc, PhD, Eng. Lidia Jasińska-Walc, for your never-ending support and trust in me. Every time I doubted myself, you knew exactly how to turn that uncertainty around and keep my chin up. From the very first moment I met you years ago in Gdańsk, I knew I wanted to work with and learn from you. Your experience, confidence, kind heart, and perseverance make you an exceptional person and leader.

I would also like to thank Prof. PhD Rob Duchateau for showing me that when it comes to research, creativity and imagination have no limits. You taught me to be more courageous, to try new things, and to follow my instincts. Your strength, trust, and ability to always get our team back on its feet are truly admirable. You also taught me the importance of constantly questioning myself, which I deeply value. Both you and Lidia will always remain important role models in my life, the people who shaped my scientific backbone.

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In addition, I would like to thank my colleagues from the SABIC T&I Center in Geleen, especially Miloud, Kenny, Bryan, Eric, Koen, Marcel, for the endless discussions, coffee breaks, good times, and help during my research. Your positive attitude and experience made my daily lab work so much more pleasant.

Curriculum Vitae

Weronika Nowicka is an early-career researcher specializing in polymer chemistry and material science, actively collaborating during her PhD with industry and international research centers. Her research interests encompass the design, synthesis, deep characterization, and application-oriented performance of functional polymers, as well as the pursuit of sustainable polymeric solutions to global plastic recycling challenges, addressing both chemical and mechanical recycling approaches.



Weronika Nowicka was born on 26th of October 1997, in Świecie, Poland, where she completed her secondary education at the high school (I Liceum Ogólnokształcące im. Floriana Ceynowy) with a biology, chemistry and English focus. Weronika earned both her Master's and Engineer's degrees in Chemical Technology at Gdańsk University of Technology cum laude, specializing in the technology of polymers, cosmetics, and functional materials. Already during her Master's studies, she conducted international research, including a long-term research internship at SABIC within the Erasmus+ Traineeship program. Her Master's thesis, titled "*Properties and Application of Functional Polymers*", was supervised by Prof. DSc, PhD, Eng. Lidia Jasińska-Walc, and served as the direct foundation for further scientific collaboration during her doctoral studies. During this internship she focused on characterization of polypropylene-based functionalized polyolefins and their commercial application as hot-melt adhesives in collaboration with Henkel Inspiration Center Düsseldorf (ICD) (Germany).

Currently, Weronika Nowicka is a 4th-year PhD candidate at the Doctoral School of Gdańsk University of Technology in the discipline of chemical sciences. Her doctoral dissertation, carried out under the supervision of Prof. DSc, PhD, Eng. Lidia Jasińska-Walc, and Prof. PhD Rob Duchateau (University of Groningen, SABIC T&I Centre), focuses on the development of novel, sustainable polymeric materials based on polyolefins within the research project entitled "*Chemically Recyclable Polyolefin Mimics*". This project forms part of an ongoing collaboration between Gdańsk University of Technology and the SABIC

Technology & Innovation Center in Geleen, the Netherlands. To date, Weronika Nowicka has an h-index of 4 (Web of Science) and 63 citations.

Research experience of Weronika Nowicka includes four subsequent research internships at the SABIC Technology & Innovation Center (Geleen, Cartagena, Bergen op Zoom, 2022–2026) and an invitation for a research stay at the University of Groningen (September 2025), where she conducted advanced rheological measurements for her PhD dissertation. The internship in Groningen also allowed her to establish valuable professional connections aimed at future scientific collaboration. She has participated in several research projects funded by SABIC and Gdańsk University of Technology, including those on the structure and functional properties of polyolefins and their application in adhesive materials.

Weronika Nowicka has been awarded numerous prestigious scholarships, including the NAWA STER grant for top doctoral students conducting research in international collaboration (2023 and 2025 editions), PROM Travel Programme Grant (2025), the Francium Program Supporting Outstanding Doctoral Candidates (2023–2025), the Polonium International Doctoral Fellowships (2022), and the Radon Program Supporting Most Talented Students (2021). She also received the Gold Badges of the Graduate of Gdańsk University of Technology for completing both degree cycles with distinction, as well as the Rector's Scholarship for top students of the Faculty of Chemistry (2017–2020).

Academic Output

Scientific Papers

Bertoncini, B., Bancalà, G., Nowicka, W., Battisti, A., Pusceddu, I., Turelli, M., Neethirajan, J., Portale, G., Duchateau, R., Adamo, C., Pucci, A., Carlotti, M.; Pyrolysis-derived telechelic polypropylene enables mechanochromic mapping of cavitation in polyolefin matrices; *Journal of Materials Chemistry C*, **2026** 14(28), 12564–12577.

DOI: 10.1039/d5tc04217h

IF₂₀₂₆ – 5.1; MNiSW – 140

Nowicka, W., Szot, W., Rozanski, A., Yang, L., Gautam, P. S., Chinta, S., Verghese, N., Duchateau, R., Jasinska-Walc, L.; Chemically Recyclable Polyester Miscible with HDPE Transforms Contamination into Functional Enhancement; *Macromolecules* **2026** 59(12), 6906–6913. Article selected for *Front Cover*.

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IF₂₀₂₆ – 5.7; MNiSW – 140

Nowicka, W., Rozanski, A., Pasha, F. A., Jasinska-Walc, L., Duchateau, R.; Polyethylene-like Polyesters: Strategies for Tailoring Mechanical Properties and Adhesion Performance; *Macromolecules* **2025** 58(17), 9440-9449.

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IF₂₀₂₆ – 5.7; MNiSW – 140

Nowicka, W., Szot, W., Jasinska-Walc, L., Duchateau, R.; High-Molecular-Weight Polyesters Mimicking Linear Low-Density Polyethylene: Mechanistic Insight and Structure–Property Relationship; *ACS Applied Polymer Materials* **2025** 7(17), 12105-12116.

DOI: 10.1021/acsapm.5c02911

IF₂₀₂₆ – 5.2; MNiSW – 20

Kruszynski, J., Nowicka, W., Pasha, F. A., Yang, L., Rozanski, A., Bouyahyi, M., Kleppinger, R., Jasinska-Walc, L., Duchateau, R.; Tuning the Adhesive Strength of Functionalized Polyolefin-Based Hot Melt Adhesives: Unexpected Results Leading to New Opportunities; *Macromolecules* **2025** 58(6), 2894–2904.

DOI: 10.1021/acs.macromol.4c02945

IF₂₀₂₆ – 5.7; MNiSW – 140

Kruszynski, J., Nowicka, W., Rozanski, A., Liu, Y., Parisi, D., Yang, L., Pasha, F. A., Bouyahyi, M., Jasinska-Walc, L., Duchateau, R.; iPP/HDPE blends compatibilized by a polyester: An unconventional concept to valuable products; *Science Advances* **2024** 10 (21), eado1944.

DOI: 10.1126/sciadv.ado1944

IF₂₀₂₆ – 13.9; MNiSW – 200

Kruszynski, J., Nowicka, W., Bouyahyi, M., Liu, Y., Yang, L., Rozanski, A., Anbuezhian, N., Jasinska-Walc, L., Duchateau, R.; Unprecedented Adhesive Performance of Propylene-Based Hydroxyl-Functionalized Terpolymers; *ACS Applied Polymer Materials* **2023** 5 (5), 3875–3882.

DOI: 10.1021/acsapm.3c00566

IF₂₀₂₆ – 5.2; MNiSW – 20

Granted Patents

1. Duchateau, R.; Jasinska-Walc, L.; Bouyahyi, M.; Kruszynski, J.; Nowicka, W.; Szot, W. *Encapsulant film based on functionalized polyolefins*. (US12622070B2)
2. Duchateau, R.; Jasinska-Walc, L.; Bouyahyi, M.; Kruszynski, J.; Nowicka, W.; Szot, W.; Gautam, P. S. *Hot melt adhesives based on blends comprising non-functionalized and functionalized polyolefins*. (EP4484516B1)

Patent Applications

1. Jasinska-Walc, L.; Bouyahyi, M.; Duchateau, R.; Kruszynski, J.; Nowicka, W. *Hot melt adhesive comprising siloxide-functionalized polyolefins*. (WO2024088806A1)
2. Jasinska-Walc, L.; Duchateau, R.; Bouyahyi, M.; Malus, M.; Sienkiewicz, M.; Soliman, M.; Yang, L.; Nowicka, W.; Szot, W. *Asphalt composition with an improved life span*. (EP4619466A1)
3. Duchateau, R.; Jasinska-Walc, L.; Kruszynski, J.; Nowicka, W.; Szot, W.; Bouyahyi, M. *Encapsulant film based on functionalized polyolefins*. (WO2024256561A1)
4. Jasinska-Walc, L.; Duchateau, R.; Bouyahyi, M.; Kruszynski, J.; Gautam, P. S.; Nowicka, W.; Szot, W. *Hot melt adhesives based on blends comprising non-functionalized and functionalized polyolefins*. (WO2025002626A1)
5. Chinta, S.; Sabnis, K.; Kannan, G.; Jasinska-Walc, L.; Duchateau, R.; Koripelly, G.; Stanislaus, A.; Narayanaswamy, R.; Soliman, M.; van den Esschert, B. A. H.; Verghese, N. K. E.; Nowicka, W. *Blends of repeatedly recyclable-polymer mimics of linear low-density polyethylene (LLDPE) polymers*. (WO2025/061946).
6. Chinta, S.; Sabnis, K.; Kannan, G.; Jasinska-Walc, L.; Duchateau, R.; Koripelly, G.; Stanislaus, A.; Narayanaswamy, R.; Soliman, M.; van den Esschert, B. A. H.; Verghese, N. K. E.; Nowicka, W. *Blends of repeatedly recyclable-elastomer copolymer mimics (RR-ECPMS) of polyolefin elastomer copolymer blends*. (WO2025/061945).
7. Chinta, S.; Sabnis, K.; Kannan, G.; Jasinska-Walc, L.; Duchateau, R.; Koripelly, G.; Stanislaus, A.; Narayanaswamy, R.; Soliman, M.; van den Esschert, B. A. H.; Verghese, N. K. E.; Nowicka, W. *Blends of repeatedly recyclable-elastomer copolymer mimics of low-density polyethylene (LDPE) polymers*. (WO2025/061947).
8. Chinta, S.; Sabnis, K.; Kannan, G.; Jasinska-Walc, L.; Duchateau, R.; Koripelly, G.; Stanislaus, A.; Narayanaswamy, R.; Soliman, M.; van den Esschert, B. A. H.; Verghese, N. K. E.; Nowicka, W. *Blends of repeatedly recyclable-polymer mimics (RR-PMS) of polypropylene polymers*. (WO2025/061948).
9. Chinta, S.; Sabnis, K.; Kannan, G.; Jasinska-Walc, L.; Duchateau, R.; Koripelly, G.; Stanislaus, A.; Narayanaswamy, R.; Soliman, M.; Jin, J.; Verghese, N. K. E.; Nowicka, W. *Repeatedly recyclable polyolefin copolymer mimics (RR-PCMS)*. (WO2025/061950).
10. Chinta, S.; Sabnis, K.; Kannan, G.; Stanislaus, A.; Narayanaswamy, R.; Soliman, M.; Jin, J.; Verghese, N. K. E.; Jasinska-Walc, L.; Duchateau, R.; Koripelly, G.; Nowicka, W. *Repeatedly recyclable-polyolefin copolymer mimics (RR-PCM)*. (WO2025/061951).

11. Chinta, S.; Sabnis, K.; Kannan, G.; Jasinska-Walc, L.; Duchateau, R.; Koripelly, G.; Stanislaus, A.; Narayanaswamy, R.; Soliman, M.; Jin, J.; Verghese, N. K. E.; Nowicka, W. *Repeatedly recyclable polyolefin copolymer mimics (RR-PCMS)*. (WO2025/061952).
12. Chinta, S.; Sabnis, K.; Kannan, G.; Jasinska-Walc, L.; Duchateau, R.; Koripelly, G.; Stanislaus, A.; Narayanaswamy, R.; Soliman, M.; Jin, J.; Verghese, N. K. E.; Nowicka, W. *Repeatedly recyclable-polyolefin copolymer mimics (RR-PCMS)*. (WO2025/061954).
13. Chinta, S.; Sabnis, K.; Kannan, G.; Jasinska-Walc, L.; Duchateau, R.; Koripelly, G.; Stanislaus, A.; Narayanaswamy, R.; Soliman, M.; van den Esschert, B. A. H.; Nowicka, W.; Verghese, N. K. E. *Blends of repeatedly recyclable-plastomer co-polymer mimics (RR-PCPMS) of polyolefin plastomer copolymer blends*. (WO2025/061955).
14. Chinta, S.; Sabnis, K.; Kannan, G.; Jasinska-Walc, L.; Duchateau, R.; Koripelly, G.; Stanislaus, A.; Narayanaswamy, R.; Soliman, M.; van den Esschert, B. A. H.; Verghese, N. K. E.; Nowicka, W. *Blends of repeatedly recyclable-polymer mimics of high-density polyethylene (HDPE) polymers*. (WO2025/061956).

Conferences

Oral Presentations

1. “*Tuning Mechanical Properties and Adhesion in Polyethylene-like Polyesters*” during Brightlands Polymer Days 2026, 20 – 21 April 2026, Geleen, Netherlands
2. “*Polyethylene-like Polyesters: Strategies for Tailoring Mechanical Properties and Adhesion*” during European Polymer Congress 2025, 22 – 27 June 2025, Groningen, Netherlands
3. “*Kompatybilne mieszaniny iPP/HDPE – od niekonwencjonalnego pomysłu do wartościowego produktu*” (*Compatible iPP/HDPE Blends – from Unconventional Idea to Valuable Product*) during 66th Polish Chemical Society Conference (PTCHEM) 2024, 15 – 20 September 2024, Poznań, Poland
4. “*Wpływ Struktury Funkcjonalnych Poliolefin na Właściwości Adhezyjne*” (*The Influence of Functionalized Polyolefins’ structure on Adhesive Properties*) during 65th Polish Chemical Society Conference (PTCHEM) 2023, 18 – 22 September 2023, Toruń, Poland

Poster Presentations

1. “*Polyester Miscible with HDPE Transforms Contamination into Functional Enhancement*” during Bordeaux Polymer Conference 2026 (BPC2026), 1 – 4 June 2026, Bordeaux, France
2. “*iPP/HDPE Blends Compatibilized by a Polyester: An Unconventional Concept to Valuable Products*” during IUPAC Macro 2024, 1 – 4 July 2024, Warwick, United Kingdom
3. “*Characterization of the Functional Polyolefins as Components of New-Generation Adhesive Materials*” during Brightlands Polymer Days 2024, 27 – 28 May 2024, Geleen, Netherlands

Author Contribution Statements

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Declaration of Co-authors' Approval and Contribution

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Entry	Type of Contribution	Publication			
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1	Writing – original draft				
2	Writing – review & editing	X	X	X	X
3	Investigation				
4	Data curation				
5	Visualization				
6	Methodology				
7	Conceptualization	X	X	X	X
8	Validation				
9	Resources				
10	Project administration	X	X	X	X
11	Funding acquisition	X	X	X	X
12	Supervision	X	X	X	X

1 – Kruszynski, J., Nowicka, W., Rozanski, A., Liu, Y., Parisi, D., Yang, L., Pasha, F. A., Bouyahyi, M., Jasinska-Walc, L., Duchateau, R.; iPP/HDPE blends compatibilized by a polyester: An unconventional concept to valuable products; *Sci. Adv.* **2024** 10(21), eado1944.

2 – Nowicka, W., Szot, W., Jasinska-Walc, L., Duchateau, R.; High-Molecular-Weight Polyesters Mimicking Linear Low-Density Polyethylene: Mechanistic Insight and Structure–Property Relationship; *ACS Appl. Polym. Mater.* **2025**, 7(17), 12105–12116.

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4 – Nowicka, W., Szot, W., Rozanski, A., Yang, L., Gautam, P. S., Chinta, S., Verghese, N., Duchateau, R., Jasinska-Walc, L.; Chemically Recyclable Polyester Miscible with HDPE Transforms Contamination into Functional Enhancement; *Macromolecules* **2026**, 59(12), 6905–6913.

I hereby confirm that I have read and understood the content of the table above, and I approve my contribution and the use of the scientific publication, of which I am a co-author, to be included in the PhD thesis of Weronika Nowicka entitled: *Chemically Recyclable Polyolefin Mimics*.

Lidia Jasińska-Walc

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1	Writing – original draft				
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3	Investigation				
4	Data curation				
5	Visualization				
6	Methodology				
7	Conceptualization	X	X	X	X
8	Validation				
9	Resources				
10	Project administration	X	X	X	X
11	Funding acquisition	X	X	X	X
12	Supervision	X	X	X	X

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3 – Nowicka, W., Rozanski, A., Pasha, F. A., Jasinska-Walc, L., Duchateau, R.; Polyethylene-like Polyesters: Strategies for Tailoring Mechanical Properties and Adhesion Performance; *Macromolecules* **2025**, 58(17), 9440–9449.

4 – Nowicka, W., Szot, W., Rozanski, A., Yang, L., Gautam, P. S., Chinta, S., Verghese, N., Duchateau, R., Jasinska-Walc, L.; Chemically Recyclable Polyester Miscible with HDPE Transforms Contamination into Functional Enhancement; *Macromolecules* **2026**, 59(12), 6906–6913.

I hereby confirm that I have read and understood the content of the table above, and I approve my contribution and the use of the scientific publication, of which I am a co-author, to be included in the PhD thesis of Weronika Nowicka entitled: *Chemically Recyclable Polyolefin Mimics*.



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3	Investigation	X			
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Entry	Type of Contribution	Publication			
		1	2	3	4
1	Writing – original draft		X		
2	Writing – review & editing				
3	Investigation		X		X
4	Data curation		X		
5	Visualization		X		
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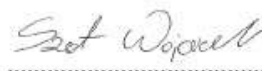
1 – Kruszynski, J., Nowicka, W., Rozanski, A., Liu, Y., Parisi, D., Yang, L., Pasha, F. A., Bouyahyi, M., Jasinska-Walc, L., Duchateau, R.; iPP/HDPE blends compatibilized by a polyester: An unconventional concept to valuable products; *Sci. Adv.* **2024** *10*(21), eado1944.

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1	Writing – original draft				
2	Writing – review & editing	X		X	
3	Investigation	X		X	
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1	Writing – original draft				
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Declaration of Co-authors' Approval and Contribution

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Signature

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Declaration of Co-authors' Approval and Contribution

Name of co-author: PhD Daniele Parisi

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1	Writing – original draft				
2	Writing – review & editing	X			
3	Investigation	X			
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Entry	Type of Contribution	Publication			
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1	Writing – original draft				
2	Writing – review & editing	X		X	X
3	Investigation	X		X	X
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Declaration of Co-authors' Approval and Contribution

Name of co-author: Lanti Yang

Entry	Type of Contribution	Publication			
		1	2	3	4
1	Writing – original draft				
2	Writing – review & editing				
3	Investigation	X			X
4	Data curation	X			X
5	Visualization				
6	Methodology				
7	Conceptualization				
8	Validation				
9	Resources				
10	Project administration				
11	Funding acquisition				
12	Supervision				

1 – Kruszynski, J., Nowicka, W., Rozanski, A., Liu, Y., Parisi, D., Yang, L., Pasha, F. A., Bouyahyi, M., Jasinska-Walc, L., Duchateau, R.; iPP/HDPE blends compatibilized by a polyester: An unconventional concept to valuable products; *Sci. Adv.* **2024** 10(21), eado1944.

2 – Nowicka, W., Szot, W., Jasinska-Walc, L., Duchateau, R.; High-Molecular-Weight Polyesters Mimicking Linear Low-Density Polyethylene: Mechanistic Insight and Structure–Property Relationship; *ACS Appl. Polym. Mater.* **2025**, 7(17), 12105-12116.

3 – Nowicka, W., Rozanski, A., Pasha, F. A., Jasinska-Walc, L., Duchateau, R.; Polyethylene-like Polyesters: Strategies for Tailoring Mechanical Properties and Adhesion Performance; *Macromolecules* **2025**, 58(17), 9440-9449.

4 – Nowicka, W., Szot, W., Rozanski, A., Yang, L., Gautam, P. S., Chinta, S., Verghese, N., Duchateau, R., Jasinska-Walc, L.; Chemically Recyclable Polyester Miscible with HDPE Transforms Contamination into Functional Enhancement; *Macromolecules* **2026**, 59(12), 6906–6913.

I hereby confirm that I have read and understood the content of the table above, and I approve my contribution and the use of the scientific publication, of which I am a co-author, to be included in the PhD thesis of Weronika Nowicka entitled: *Chemically Recyclable Polyolefin Mimics*.

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 Signature

Date: 08.07.2026

Declaration of Co-authors' Approval and Contribution

Name of co-author: Siva Chinta

Entry	Type of Contribution	Publication			
		1	2	3	4
1	Writing – original draft				
2	Writing – review & editing				
3	Investigation				
4	Data curation				
5	Visualization				
6	Methodology				
7	Conceptualization				X
8	Validation				
9	Resources				X
10	Project administration				X
11	Funding acquisition				X
12	Supervision				

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Signature

Date: 08.07.2026

Declaration of Co-authors' Approval and Contribution

Name of co-author: Pankaj S. Gautam

Entry	Type of Contribution	Publication			
		1	2	3	4
1	Writing – original draft				
2	Writing – review & editing				
3	Investigation				
4	Data curation				
5	Visualization				
6	Methodology				
7	Conceptualization				X
8	Validation				
9	Resources				X
10	Project administration				X
11	Funding acquisition				X
12	Supervision				

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Due to the P. S. Gautam having departed SABIC and being unreachable, I hereby confirm that the statements provided herein are true and accurate.

Lidia Jasinska-Walc

Signature

Date: 08.07.2026

Declaration of Co-authors' Approval and Contribution

Name of co-author: Nikhil Verghese

Entry	Type of Contribution	Publication			
		1	2	3	4
1	Writing – original draft				
2	Writing – review & editing				X
3	Investigation				
4	Data curation				
5	Visualization				
6	Methodology				
7	Conceptualization				
8	Validation				
9	Resources				X
10	Project administration				X
11	Funding acquisition				X
12	Supervision				

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Due to the N. Verghese having departed SABIC and being unreachable, I hereby confirm that the statements provided herein are true and accurate.

Adia Jasinska-Walc

Signature