Hebrew Abstract

השבחת פסולת תרמופלסטים בתהליכים קטליטיים משולבים כימיים וביולוגיים

רינה טננבאום

המאמר מתאר תהליך חדשני שיאפשר סינתזה של פולימרים ממוחזרים בעלי ביצועים גבוהים (HPRP) ממונומרים שעברו שדרוג ומקורם בפסולת פלסטיק. נתמקד בפוליאולפינים, קבוצת פלסטיקים שקשה במיוחד לפרק בשל קשרי C–C ו-C–H האינרטיים שלהם. ייצור מונומרים שעברו שדרוג מפסולת פוליאולפינים באמצעות תהליכים כימיים חסכוניים ובתנאים מתונים, בניגוד לשיטות בטמפרטורות גבוהות ובעלויות גבוהות, הוא בעל חשיבות מכרעת, ויאפשר סגירת המעגל של כלכלת הפלסטיק המעגלית. ה-HPRP החדשים שיפותחו ירחיבו את מרחב התכנון של חומרים פלסטיים, ויציעו הזדמנויות עשירות למחקר מדעי ולפיתוח יישומים חדשניים.

האסטרטגיה שהמאמר מתאר לחיסול פסולת פלסטיק כוללת דה-פולימריזציה קטליטית כימית של פסולת פוליאולפינים לשברים קטנים בטמפרטורות נמוכות יחסית, הפיכתם למונומרים שימושיים באמצעות שדרוג ביולוגי בעזרת מערכי אנזימים שתוכננו במיוחד, סינתזה של פולימרים חדשים, ממוחזרים ובעלי ביצועים גבוהים, ואפשרות למחזורם הקל והיעיל, ובכך לאפשר מעבר לכלכלה מעגלית.

מילות מפתח: פסולת פלסטית, שדרוג חומרים, תהליכים קאטליטיים, כלכלה מעגלית.

Rina Tannenbaum

Upcycling of Waste Thermoplastics by Chemical and Biological Hybrid Catalytic Processes

Abstract

We describe here an innovative process that will enable the synthesis of *high-performance recyclable polymers (HPRP)* from upcycled monomers originating in waste plastic materials. We will focus on polyolefins, a class of plastics that are particularly difficult to break down due to their inert C-C and C-H bonds. Producing upcycled monomers from waste polyolefins through cost-efficient chemical processes at mild conditions, as opposed to high-temperature/high-cost methods, is of pivotal importance and will enable closing the loop of plastic circularity. The newly designed HPRP will augment *plastic materials design space* and offer rich opportunities for scientific exploration and the development of novel applications.

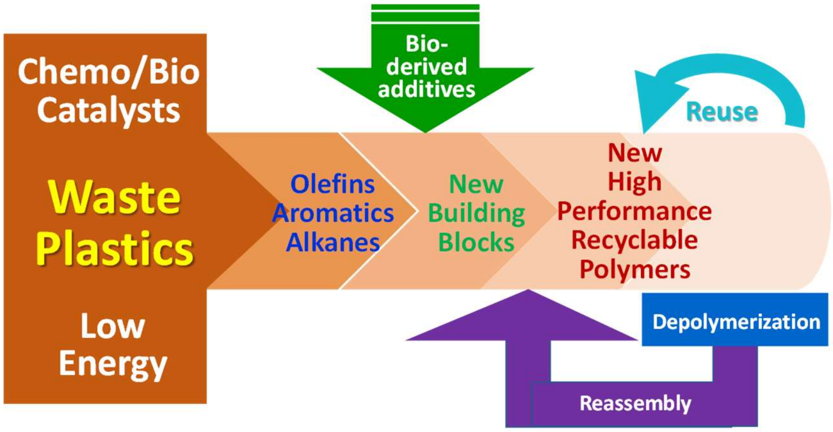
The strategy that we describe to eliminate plastic waste involves the chamical catalytic depolymerization of waste polyolefins into small fragments at relatively low temperatures, functionalize them into useful monomers by biological upcycling with especially tailored enzymatic cascades, synthesize new, high-performance recyclable polymers, and enable their facile recycling and provide a transition to *a circular economy.*

Keywords: Plastic waste, High-performance recyclable polymers Polymers (HPRP), Upgrading materials, Catalytic processes, Circular Economy.

1. Introduction

The upcycling of waste thermoplastics into novel green polymers through chemical and microbial processes is an innovative approach to addressing the global challenge of plastic waste. This method not only helps in reducing the environmental impact of plastic waste but also contributes to the development of high-performance recyclable materials. A schematic of the overall process is shown in **Figure 1**.

Figure 1: Schematic vision of the chemical/biological hybrid catalyzed upcycling of waste plastic to form high-performance recyclable polymeric materials.



While polyolefins, including polyethylene (PE) (both high density PE or low density PE), and polypropylene (PP), are the largest class of thermoplastics produced globally, their chemical recycling/upcycling ratio is inferior to other plastics.[1-4] One can expect that their low recycling ratio is mainly due to their almost inert chemical structures, solely composed of single C-C and C-H bonds, unlike other plastics containing functional groups, such as ester, amide, and carbamate groups that can facilitate the multiple scission reactions under relatively mild conditions. Nonetheless, one most intensively studied method to break these robust bonds and convert polymer into smaller molecules, including liquid and gas products, is catalytic or non-catalytic pyrolysis with thermal energy input that is high enough to overcome the energy barrier of conversion. While the pyrolysis of polyolefins could produce a high yield of liquid hydrocarbons with varying levels of saturation, typically more than 80% of yield, this process is highly energy-intensive and makes it difficult to produce commercially viable high value-added chemicals due to the frequent failure of product control. The common products generated from pyrolysis are complex compounds, including a wide range of hydrocarbon gas, oil, wax, and char.[5-7] The low-valued products result mainly from the uncontrolled chain cleavage or cross-linking reaction by the generated radical species at high temperatures. Therefore, the design of new catalysts that can cleave C-C bonds effectively and selectively under mild reaction conditions is urgently needed to produce high-quality liquid products with a narrow distribution of hydrocarbon chains by lowering both operation and separation costs.

The transformation of waste plastic into high-performance recyclable materials involves a closed-loop hybrid chemical/biochemical process. This process aims to develop novel hybrid chemical and microbial catalysts to selectively break down mixed thermoplastics into small molecular fragments (monomers). These monomers are then in turn transformed into high-value chemical building blocks through microbial bio-funneling techniques. The resulting high-performance biopolymers and composites are designed to optimize their performance for various applications, such as additive manufacturing (3D printing).

2. Educational and Societal Aspects

The interdisciplinary research described in this review consists of a transformative strategy for the novel, cost-effective, and environmentally friendly chemical and biological processes to deconstruct waste thermoplastics, and use the transformed molecules to design, model, manufacture, and characterize new sustainable polymers and nanocomposites for a variety of applications, such as high-performance recyclable materials and additive manufacturing. The research is a result of a synergistic approach of experiments and theory, which required the collaboration of a diverse team of experts. The knowledge base created by this research will lead to new economical and sustainable materials, advancements in the development of novel, high-performance materials and processes, and new methodologies for accelerating the transition from innovation to industrial implementation.

The work described in this review addresses the global challenge of beneficial reuse of waste plastics. The development of these green plastics out of waste toxic materials will open a broad scope of applications, spanning education, medicine, energy, transportation, and others. The innovative multi-disciplinary nature of this research, as it expands globally, will require adjustments and innovations in the curriculum at all levels of the educational hierarchies, combining coursework, laboratory training, and industrial immersions and will accelerate the progress and train the workforce to lead these efforts. The work described in this review will provide rich synergistic interdisciplinary research experiences for students and researchers at all levels, intended to tackle global plastic issues and promote novel career opportunities, create a deeper awareness of plastic waste's impact on health, environment, and economy, and engage the public to adopt better policies to battle global plastic waste.

3. The Hybrid Chemical/Biological Upcycling Process

The hybrid chemical/biological upcycling process is applied to common mixed plastics like polyurethane (PU), polycarbonate (PC), and polyethylene terephthalate (PET) or mixtures of polyolefins. The process involves the combination of petroleum-based, synthetic, plastic-derived monomers to develop high-value, high-performance polymers and composites. These novel polymers are designed to be easily recyclable, thus enabling a circular materials economy.

1.1. Catalytic Fragmentation of Polyolefins

Polyolefin deconstruction can be achieved using novel low-temperature catalysts that break long polymer chains into smaller fragments suitable for biological conversion. Early studies using organometallic catalysts, such as zirconium hydride on silica–alumina, showed effective fragmentation of polyethylene (PE) and polypropylene (PP) via β-alkyl elimination and hydrogenolysis at 150 - 200°C, far below conventional pyrolysis temperatures (>400°C).[8-10]

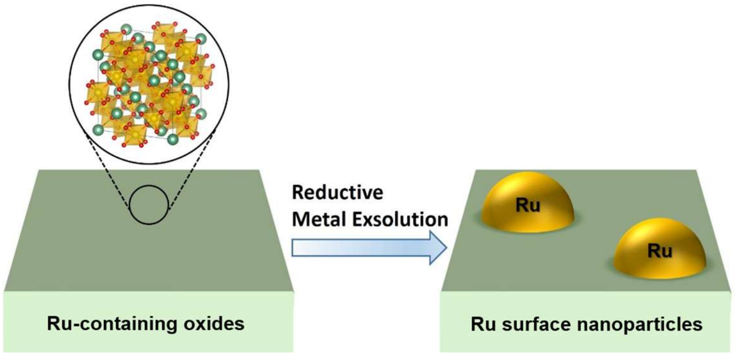
Current leading routes, catalytic hydrogenolysis and alkane metathesis, efficiently produce high-quality liquid products with narrow oligomer distributions. For instance, Pt nanoparticles on $SrTiO_3$ yield C_{42}-C_{70} hydrocarbons, while tandem Ir- or Pt-based catalysts coupled with $Re_2O_7/\gamma\text{-}Al_2O_3$ enable alkane metathesis to form C_7-C_{38} liquids at similar temperatures. $Pt/\gamma\text{-}Al_2O_3$ can also convert HDPE and LDPE into alkyl aromatics (~C_{30}).

However, these methods rely heavily on costly noble metals (Pt, Ir, Re) for their stability under molten PE conditions. Alternative systems using nickel-based catalysts and oxidants such as mCPBA show potential but are limited by PE solubility (>4 kg/mol). Mild oxidation with $Co(acac)_2$ or $Mn(acac)_2$ under low O_2 pressure (8 bar) can degrade PE (~500 kg/mol) into oxidized waxes (~10 kg/mol).

Hydrogenolysis, i.e. C-C bond cleavage with hydrogen addition, is the key pathway for mild PE deconstruction. However, only noble metals like Pt, Ir, Rh, and Ru effectively catalyze this reaction in nonfunctionalized systems. Recently, Ru/C has shown high activity and stability, converting LDPE into C_7-C_{45} alkanes (45% yield) at 200 - 250°C under 20 bar H_2. Given its lower cost than Pt, Ru-based catalysts are particularly promising.

A very promising class of Ru-based catalysts may be synthesized via the **exsolution synthesis** method. This method allows the embedding of Ru nanoparticles within oxide hosts, which then exsolve under reducing conditions to form stable, strongly anchored Ru nanoscale species, as shown in **Figure 2**.

Figure 2: Schematic description of the exsolution synthesis method, which allows the embedding of Ru nanoparticles within oxide hosts to form stable, strongly anchored Ru nanoscale species

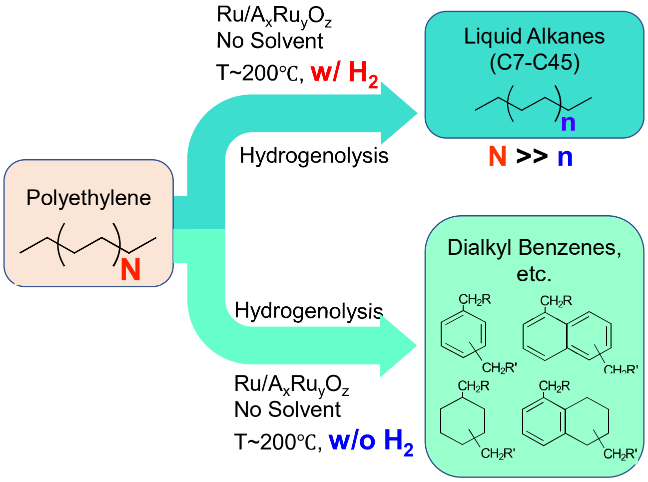


This technique minimizes sintering, allows precise stoichiometric control, and has proven durability under harsh oxidative environments. Building on this development it is possible to generate Ru-based pyrochlore and perovskite catalysts ($Rux/ABO_3-\delta$) and investigate their applicability as the first stage in the chemical deconstruction of polyolefins. The main issues to address are the hydrogenolysis pathways with and without Ru-oxide supports and the synergistic effect of Ru metal–oxide interfaces. [11-15]

Two main deconstruction products may be identified and are shown in **Figure 3**: (a) Liquid alkanes (C_7-C_{45}) are generated via hydrogenolysis under H_2, and (b) Alkyl aromatics are generated via hydrogenolysis-aromatization without H_2, both solvent-free. Subsequently, the overall strategy for generating of upcycled functionalized monomers from the catalytic deconstruction products of PE will involve two different routes, shown in **Figure 4:**

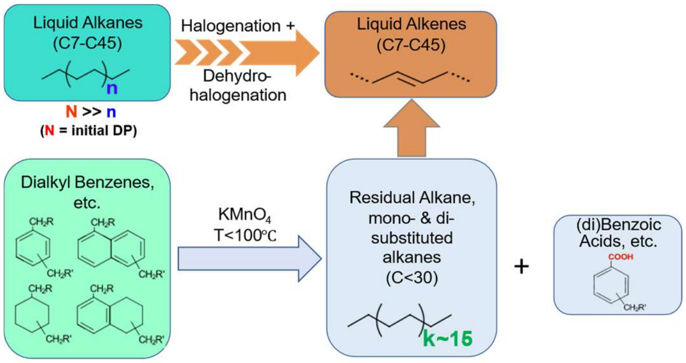
(1) Generation of short chain olefins (alkenes) by the halogenation (chlorination) and subsequent dehydrohalogenation of the alkanes formed in **Figure 3**.

Figure 3: The chemically-catalyzed hydrogenolysis of polyolefins with and without the presence of hydrogen.



These alkenes may can be further cleaved via oxidation to form (di)carboxylic acids. To create a "point of oxidation" in the long chain linear alkanes (~C30), double bonds are needed throughout the alkyl chain, amenable to subsequent oxidations, to generate monomers to be utilized subsequently for green polymers. Many chlorination methodologies are available, with the most prevalent being the Cl_2 gas used as the feed, or generated in situ, which will pose a severe health hazard. We propose to employ a mild chlorination condition, demonstrated for low molecular weight PE (Mn ~ 4 kg/mol) that would offer a mild and tunable approach to obtain a chlorinated alkane, with a Cl addition efficiency of 98% to 37%. The weight percent of halogen incorporated varies,[35] depending on the feed ratios utilized, and this methodology would provide the much-needed knob to tune the amount of double bond that is subsequently formed. This approach will allow tuning the amount of double bond formed in the next step and enable the formation of long-chain diacids, di ketones (C10+), etc., inaccessible via other routes. The extent of chlorination will be evaluated via spectroscopic techniques (FTIR, NMR) and elemental analysis.

Figure 4: The overall strategy for the generation of upcycled functionalized monomers from the first step of the catalytic deconstruction products of polyolefins.



The subsequent dehydrohalogenation of the chlorinated alkanes is generally efficient in the presence of a base (NaOH, KOtBu, and others), and the reaction efficiency increases with temperature. Such transformations were demonstrated for the dechlorination of polyvinyl chloride (PVC), a case even more challenging than a randomly chlorinated alkane, due to vicinal chlorine atoms and heavily chlorinated chains. Other approaches of efficient dechlorination methodologies utilize ionic liquids at temperatures up to 180°C. The conditions must be tuned to maximize elimination while minimizing substitution. The use of lower base concentrations in polyethylene glycol (PEG) with molecular weights between 200-800 g/mol systems has been demonstrated for the elimination of HCl in PVC. A similar approach will be employed in this work to obtain olefins.

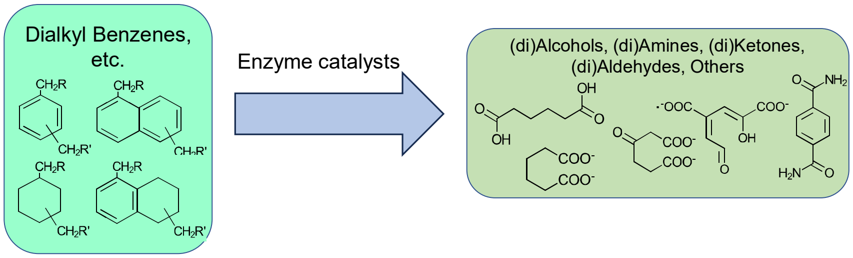
(2) The alkyl aromatic compounds generated in **Figure 3** may be converted into functional compounds such as (di)benzoic acids, etc., with the aid of various oxidants, such as $KMnO_4$, peroxy acid, and ozone. The obtained (di)benzoic acids, containing reactive carboxylic group(s) at either/or both ortho-, meta-, and para-position, are intrinsically functionalized products, and, thus, they will be further used as chemical building blocks for the generation of high performance recyclable polymers (HPRP) in a circular design. If monoalkylated carboxylates are obtained, they will be utilized in capping condensation polymerizations, and essentially terminating the chain growth, as desired. If aldehydes (ketones) are obtained, they can be further transformed into olefinic compounds generating vinyl monomers for crosslinking unsaturated polyesters. Similarly, olefins obtained from the previous step will be oxidized to generate long-chain dicarboxylic acids

1.2. Enzymatic Cascades for Upcycled Monomers

Enzymatic cascades play a crucial role in the generation of upcycled monomers for high-performance recyclable polymers (HPRP). For instance, the tested cofactor self-sufficient enzyme cascade generates cis,cis-muconate from terephthalate. Similarly, artificial self-sufficient enzyme cascades are used to generate p-xylylenediamine from polyethylene-derived terephthalate.

Recently, commercially applicable and efficient enzyme-based (cell-free) technologies have been developed to enable plastic recycling. In addition, researchers have demonstrated hybrid enzyme and whole-cell microbe–based plastic upcycling strategies. However, whole-cell systems are hampered by numerous factors, including complex genetic regulation, chemical stresses from substrates/intermediates/products, culture conditions, and the difficulty of achieving commercially relevant yield, titer, and rate. In contrast, enzyme-cascade–based plastic upcycling offers several advantages due to its tunability and ability to achieve high yields of desired products by controlling and shifting unfavorable reaction equilibria. Artificial enzyme cascades can extend the synthetic capability of biosystems to produce non-natural organic molecules. Linear cascade reactions eliminate the tedious isolation and purification of intermediates, providing significant advantages over traditional stepwise synthesis.47 Cost-effective linear artificial enzyme cascades have already been developed for the upcycling of biomass-derived substrates.[16-20]

Figure 5: An example of the enzymatic linear cascade upcycling process of dialkyl benzene species into monomers capable of undergoing condensation polymerization to into high performance recyclable polymers.

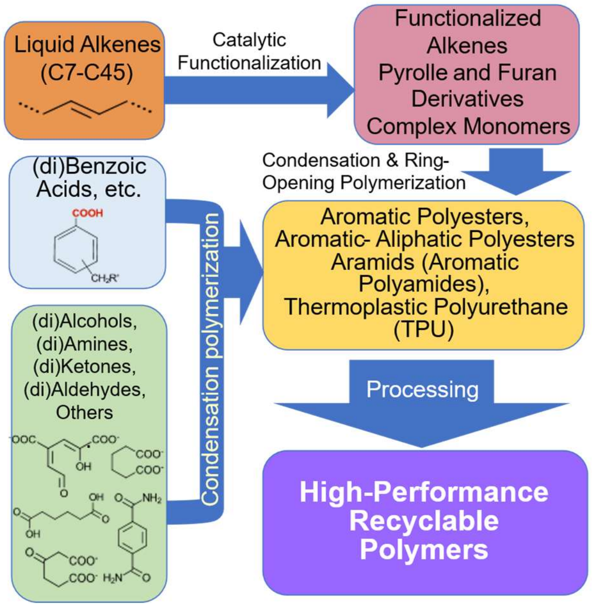


Preliminary experiments have confirmed the **in vitro** conversion of terephthalic acid to muconate using an artificial linear enzyme cascade. These preliminary results indicate that artificial linear enzyme cascades can be developed for plastic upcycling, as shown in **Figure 5**. Several enzyme cascades enable the formation of the desired monomers, using transformations derived from known metabolic pathways.[54–62] After obtaining the required native or engineered enzymes and determining their kinetic parameters, reactions are scaled and run in controlled bioreactors (5–10 L) to generate monomers. Products are be purified using efficient downstream methods and delivered to be transformed into high-performance recyclable polymers.

4. Synthesis of High-Performance Recyclable Polymers (HPRP)

The synthesis of green, high-performance recyclable polymers involves the copolymerization of upcycled monomers. The goal is to create HPRPs that can be depolymerized back to their original or equivalent building blocks, supporting a circular carbon economy. Condensation polymers, especially polyesters, polyamides, and polyacetals, are ideal candidates, because they can often be hydrolyzed under mild conditions. Difunctional monomers (diacids, diols, diamines) serve as classic building blocks, including aromatic monomers that enable high-performance materials like aramids. Polymer properties may be tuned through copolymerization, blending, and reinforcement using renewable additives such as nanocellulose or nanoclays. The overall process is shown in **Figure 6**.

Figure 6: The overall reaction requences for the synthesis of high-performance recyclable polymers from upcycled monomers following the various chemical and biological hybrid catalytic processes.

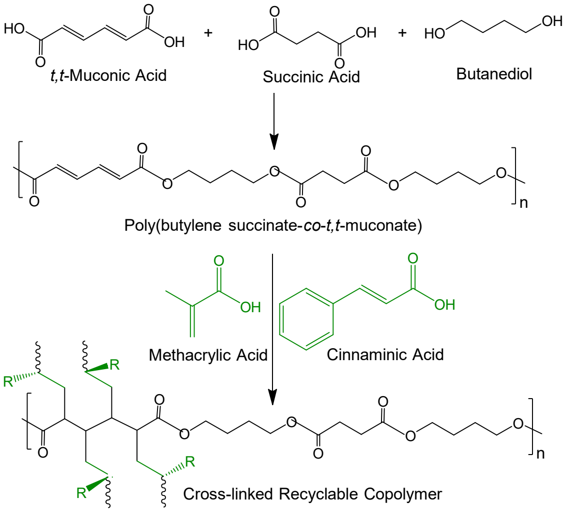


The wide range of monomers produced from polyolefin deconstruction offers many polymer design possibilities. To manage this space, we will focus on condensation polymers that replicate or surpass key properties of polyethylene (HDPE, LDPE, LLDPE, PEX), including crystallinity, viscosity, hydrophobicity, and stiffness. Polyethylene combines low processing temperatures with high crystallinity, a combination which is difficult to achieve in condensation polymers that typically have higher Tg and Tm. The aim is to match all PE benchmark properties and develop HPRPs with superior performance. The upcycled monomers produced by the chemical and enzymatic deconstruction processes are variants of uni-, di- and multifunctional monomers, which lend themselves to condensation polymerization reactions, generating recyclable materials with properties that are potentially comparable or superior to existing, petroleum-based counterparts. The classical mechanism involves the acid-base polycondensation reaction between organic acid functional groups and organic base functional groups, with the formation of ester or amide bonds, depending on the type of organic base group used (amines or alcohols). The addition of uni-functional monomers leads to chain termination, while multifunctional monomers lead to branching and a rapid increase in molecular weight. Moreover, this polymerization approach lends itself to the synthesis of a variety of polymeric species. The presence of unsaturated bonds in the polymer main chain allows the possibility of further reactions that enable the formation of crosslinks, resulting in thermoset resins. A higher density of aromatic-containing monomers contributes to the elevation of Tg, degree of crystallinity, melting point, and stiffness.[21-27]

4.1. Condensation Polymerization of Unsaturated Polyesters

Copolymerization of two different types of diacid monomers with common diols. The preferred two acid monomer species would include an aliphatic saturated monomer and an unsaturated monomer to form unsaturated polyesters. The unsaturated polyesters formed can be subsequently subjected to crosslinking with a hydrophobic vinyl monomer, such as styrene, or custom-made olefins made from monofunctional aldehydes and ketones obtained by the processes described previously. Most commercial unsaturated polyester resins (UPR) are derived from phthalic and maleic acids as the saturated and unsaturated components, both obtainable from the processes described earlier. Unsaturated polyesters are typically low-molecular-weight prepolymers. To fully cure them, they are dissolved in a vinyl monomer together with an appropriate organic peroxide as initiator and poured, sprayed, or molded into the final product and then converted into a thermoset by heating. When polymerized in the presence of unsaturated polyester, it reacts with the double bonds of the prepolymer but also undergoes homo-polymerization. An example of such a system, shown in **Figure 7,** is the co-polymerization of *trans,trans*-muconic acid with succinic acid using butanediol as the ***common diol monomer*** to form poly(butylene succinate-*co-t,t*-muconate).

Figure 7: Formation of linear and cross-linked unsaturated polyesters.

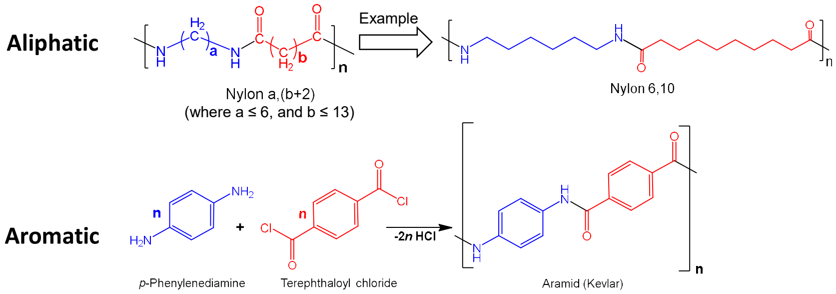


Properties may be manipulated by varying the ratio between the muconate and succinate moieties, particularly since increased muconate fraction has the effect of increasing Tg, the crystallinity and the modulus of the co-polymer due to the increased rigidity imparted by the double bonds and the trans,trans conformation of the muconic acid that allows tight packing of the polymer chains. Cross-linking in this system can be achieved by the conventional use of the hydrophobic styrene monomers, or by a novel hydrophobic olefinic monomer to impart the desired hydrophobicity, that would render the cross-linking portion of the resin more amenable to facile recyclability. A traditional unsaturated polyester synthesis example is shown in **Figure 7**. Many other glycols and acids can be used to tailor the properties of unsaturated polyesters. For example, isophthalic acid (IPA) and terephthalic acid (TA) are sometimes chosen to achieve better thermal and chemical resistance, whereas long-chain aliphatic acids, such as adipic or succinic acid, improve the flexibility but reduce the chemical and heat resistance. Vinyl monomers other than styrene and difunctional vinyl monomers such as diacrylates and dimethacrylates, can be utilized to tune properties.

4.2. Condensation Polymerization of Aliphatic and Aromatic Polyamides

A second class of technologically relevant condensation polymers obtained from monomers generated through our hybrid degradation process is comprised of polyamides, which provide a rich array of compositions and architectures, and which could exhibit a wide range of mechanical properties that could be tailored to match our benchmarks, even though the nature of polyamides is generally hydrophilic. This class of materials may be divided into two categories: aliphatic polyamides, such as nylon and its derivative, and aromatic polyamides such as phthalamids or aramids, as shown in **Figure 8**.

Figure 8: Aliphatic and aromatic polyamides HPRPs



Various types of nylon compositions may be obtained from various diamines and dicarboxylate monomers. For example, Nylon 6,10 generated from the polycondensation of hexamethylene diamine and sebacic acid, is similar in most properties to the common Nylon 6 and Nylon 6,6, but has better resilience and room temperature toughness, and lends itself for filament fabrication. Control and variations of the acid and base molecular size may provide a design tool for modulating material characteristics. While the monomer upcycling cascade that was detailed previously can generate diamines with a chain length of up to only C6, the size of diacid chains can be larger, up to C15. Therefore, since the size of the segments can be manipulated, it is possible to manipulate, to a degree, the hydrophobic nature of the polymer.

4.3. Condensation Polymerization of Unsaturated Polyamides

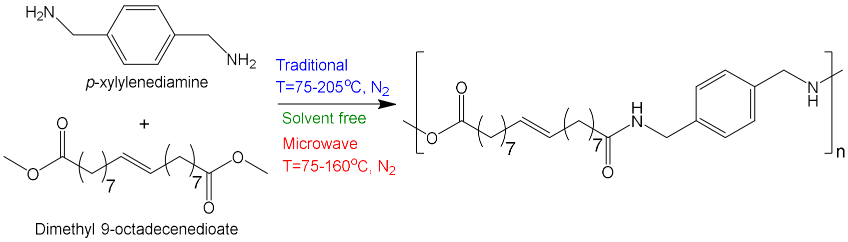
The third type of polymers of interest are unsaturated polyamides. The rationale for developing these polymers is similar to that applied for unsaturated polyesters, i.e., providing the ability to manipulate the polymer architecture by varying the ratio between the saturated diacid and the unsaturated diacid molecules, and affording the further crosslinking of the polymer and generating a thermoset resin. In addition to these attractive features, the amide bond is more resistant to hydrolysis than the ester bond. Hence, a decrease in hydrophilicity is in line with the benchmarks that we seek. There are two avenues for the synthesis of unsaturated polyamide:

(i) The modification of the synthesis of unsaturated polyesters by substituting the diol monomers with diamine monomers. As previously stated, all the monomers will be made available through the upcycling processes described previously.

(ii) Using a long chain unsaturated diacid derived from biomass (according to the schematic of our overall vision depicted in **Figure 1**), such as dimethyl 9-octadecenedioate (DMOD) derived from canola oil.

The synthesis of DMOD was reported to occur through methanolic transesterification of canola oil followed by cross-metathesis of the resulting unsaturated methyl esters in a solvent-less reaction and a product purity of > 99%. The reaction is shown in **Figure 9**. We will explore the substitution of the *p*-xylylenediamine with *p*-phenylenediamine in this reaction, as the latter will most likely have the effect of increasing chain rigidity and crystallinity.

Figure 9: Synthesis of unsaturated polyamides



4.4. Other Technologically Relevant HPRP Systems

4.4.1. Polymerization of Aldehydes

Aldehyde polymerization yields polyacetals with inherently degradable backbones. Recent advances enable controlled polymerization of o-phthalaldehyde, glyoxylate esters, and alkanals. Our previous work shows glyoxylate esters can be polymerized using protic initiators and weak bases to produce low-dispersity polymers and block copolymers.

Aldehydes sourced from catalytic or biocatalytic polyolefin degradation (alkanal, benzaldehyde, and multifunctional aldehydes) will be used to synthesize linear and crosslinked polyacetals. Target polymers will mimic polyolefin physical properties while enabling recyclability via thermal or catalytic depolymerization.

4.4.2. Synthesis of Upcycled and Value-Added Vitrimers

Vitrimers are thermoset polymers that possess exchangeable bonds, allowing reconfiguration of network topology in modes comparable to traditional thermoplastic resins. Uses of this concept include step-wise assembly of large composite structures through welding, rapid on-demand and reversible adhesive bonding, rework, and several potential routes for recyclability. Vitrimeric resins were initially produced as model compounds and composites based on the product stream from the upcycling process. Recycled monomer stream vitrimeric resins and composites will be examined for thermal, and mechanical properties, such as their interlaminar fracture toughness and interlaminar shear strength. Compressive properties of the neat vitrimeric resin will be assessed before and after the resin has been mechanically/thermally reprocessed. [28-30]

4.4.3. Technologically Important Green Polymers

Several technologically-important green polymers are synthesized through the ring-opening polymerization of upcycled cyclic esters. These include poly(D,L-lactide-co-glycolide) and mixtures of D,L-lactide and caprolactone. The resulting polymers have a multitude of architectures, ranging from block to random copolymers, depending on the monomer ratio, sequence of monomer addition, and reaction initiator.

5. Conclusions

The upcycling of waste thermoplastics through chemical and biological processes presents transformative strategies for the beneficial reuse of plastic waste. These processes enable the design, modeling, manufacturing, and characterization of new polymers and nanocomposites for sustainable manufacturing of high-performance recyclable polymers. By addressing the global challenge of plastic waste, these innovative approaches contribute to a circular materials economy and a more sustainable future.

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