

Polymer Recycling
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Towards a Cradle-to-Cradle Polyolefin Lifecycle

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Abstract: Achieving efficient chemical depolymerization of waste polyolefins to monomers remains an unsolved challenge, while it could be an effective means to avoid further waste accumulation in the environment and generate economic benefits. In a recent publication by Conk et al., polyethylene (PE) is converted to propylene, the second most used monomer in the polymer industry. The conversion is achieved via a tandem catalysis approach in which partially unsaturated PE chains react with ethylene to generate propylene with yields as high as 87%. The study is a first proof of concept showcasing a selective chemical depolymerization of PE to a monomer. Future research is expected to focus on the catalyst optimization, process design, and compatibility with contaminated and multi-polymer waste streams.

Global plastic recycling rates are extremely low with only an estimated 9% of all of plastic ever made recycled.^[1] This has led to the accumulation of plastic waste in landfills and in the environment, which is not only harmful to nature, but also to human health. This requires a multi-pronged solution, including new policies and deep societal changes, less complicated plastic product design (e.g., avoiding multi-layer materials), better collection and sorting infrastructure, novel plastics that are safe and circular by design and profitable recycling processes, to name a few.

Profitable recycling techniques can create crucial incentives to collect and sort rather than discard plastic waste. Mechanical recycling techniques are attractive, because of a relatively low energy demand and thus CO₂ footprint,^[2] but are usually not able to produce food contact materials, as additives and other potentially toxic contaminants cannot be removed in full. In addition, final polymer properties are hard to control because the high strain and heat during extrusion degrade the polymer chains.^[3] Pyrolysis is another option which has the benefit of being compatible with some

degree of contamination and mixed polymer waste streams. However, products with rather low value result, require upgrading steps which are comparable in complexity and energy demand to crude oil upgrading.^[4]

Depolymerization, where monomers are the sole final products, is an appealing approach^[5] that would result in liquid or gas, depending on the polymer, enabling the removal of contaminants and non-polymer components. This would allow for the virgin-grade production of polymers but also for circularity. While depolymerization was already demonstrated for polyesters and polyamides at pilot scale, selective cleavage of the very stable C–C bond in polyolefins is significantly more challenging. An example for high monomer selectivity was 45 wt.% for ethylene from a low linear density polyethylene (PE) feed, achieved via a high temperature two-step pyrolysis/catalytic cracking process.^[6]

The recent publication by Conk et al.^[7] brings us a step closer to the goal of selective depolymerization. By using a tandem reaction strategy, the study demonstrates that PE can be depolymerized to propylene with yields as high as 87% (Figure 1A). Excitingly, the method is robust enough to directly convert some postconsumer PE waste materials (e.g., milk bottle, shampoo bottle) to propylene with yields up to 57%. Propylene is not the monomer of PE but of polypropylene and is also used as feedstock for propylene oxide. Like ethylene, propylene is traditionally produced from steam cracking of naphtha (Figure 1B).^[8] While currently, propylene is mostly produced as by-product of ethylene production, there is a demand for new on-purpose production processes.^[9]

The described approach consists of three essential steps (Figure 1A):

- 1) A dehydrogenation step to introduce unsaturation in PE.
- 2) An isomerization step to shift the unsaturation to the desired position.
- 3) A metathesis step in presence of light alkenes to cut down the polymer chain.

The work builds upon a previously reported tandem catalysis approach, in which PE was depolymerized to light alkanes (C₃–C₇ and C₉–C₂₂, mainly) and waxes via metathesis with hexane.^[10,11] The crucial step in the new study lies in carefully choosing the ideal metathesis-partner, ethylene, instead of an alkane as in previous works to exclusively form propylene. It is worth noting that for each propylene molecule produced, two carbon atoms originate from ethylene and one from the PE backbone leading to a 33 wt.% recycling content in propylene. Combined with an ethylene production unit, this approach could be a promising

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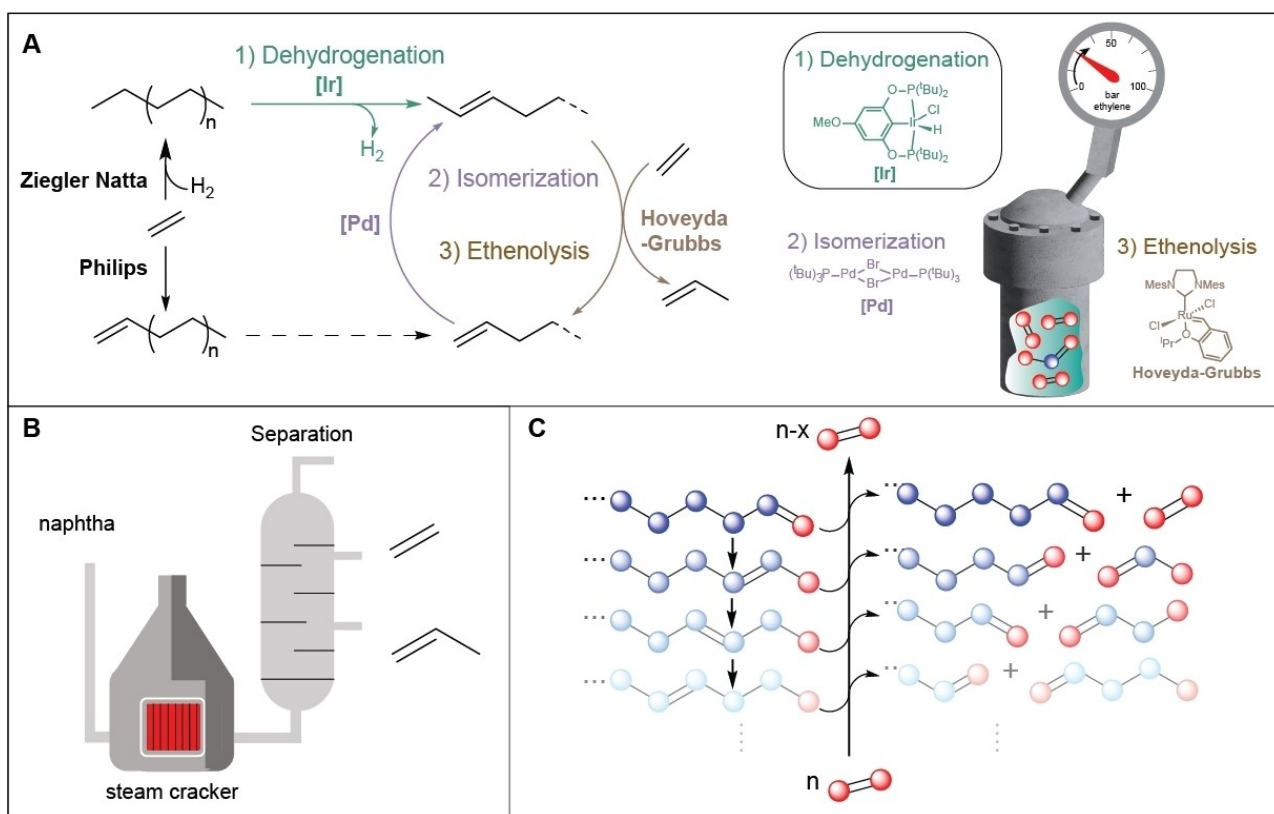


Figure 1. (A) Overview of the employed PE depolymerization strategies to propylene; (B) steam cracking of naphtha with separation unit, yielding to predominantly ethylene and propylene; (C) isomerization/ethenolysis paradigm.

way to upcycle waste PE while responding to the increasing demand for propylene.

Combining three very different reaction steps in one pot is challenging due to incompatibilities between catalysts, reaction conditions as well as chemo-selectivity issues. In that regard, the authors successfully managed to combine the isomerization and metathesis step. The dehydrogenation step was most efficiently performed separately at 200 °C; a temperature at which Grubbs metathesis catalysts are not stable.

Carefully controlling the degree of unsaturation in PE is important for the subsequent steps. Conk et al. found an optimum selectivity for propylene at a relatively low unsaturation degree (1.9 %) for HDPE. This was explained by investigating tandem catalysis on various model compounds, which showed that a high unsaturation degree leads to the formation of conjugated 1,3-dienes, which could act as a poison for one or both catalysts in steps 2 and 3.

In the next step, the balance between isomerization and metathesis rates is crucial to achieve high selectivity toward propylene. After each metathesis step, the double bond is at the end of the chain and has to be isomerized to the second position (Figure 1C). If the isomerization is much faster than the metathesis, the double bond will propagate to a position further along the chain and larger alkenes will result as was previously predicted.^[12] To achieve high propylene selectivity, a more than 100-fold excess of ethylene is used to promote metathesis reaction rates. This undoubtedly leads

to lower concentration of propylene in the product stream, but well-known ethylene/propylene separation techniques can be used to address this issue.^[13]

Apart from difficulties in combining the isomerization and metathesis reactions, further optimization is needed for the individual catalysts as well. A comprehensive screening revealed that the Hoveyda-Grubbs catalyst leads to yields significantly higher than with other Ru-based ethenolysis catalysts. However, the turnover numbers remain relatively low. This could be due to difficulties in converting such a large substrate molecule. Especially, high molecular weight polymers are expected to hinder catalysis due to the low solubility of the polymers in common solvents and the high resulting solution viscosity, slowing the diffusion of catalysts to reactive sites. In this regard, the authors' results on the dehydrogenation at higher temperatures could be interesting as they show a molecular weight decrease, most likely from random chain scissions, that could improve catalyst access to the unsaturation in the polymer chain without having any effects on the selectivity toward propylene.

Further research could focus on ways to perform this reaction in a continuous fashion. A semi-continuous process was already shown to be possible by Wang et al.,^[14] flowing ethylene continuously through the reactor, leading to a propylene yield of 27 % over 5 h. These authors also explore a heterogeneous isomerization/metathesis catalyst system in combination with a dehydrogenation catalyst in one pot, which is more stable compared to the two-step homoge-

neous system but at much decreased reaction rates. In addition, it is demonstrated that existing alkenes remaining from termination of PE, polymerized by a Philips catalyst, can be utilized as starting materials for the isomerization/metathesis step (Figure 1A).^[14]

Finally, compatibility with contaminated and mixed plastic waste streams also needs to receive further research attention. While Conk et al. successfully applied the tandem depolymerization to some waste items, other possibly multi-layer food packaging resisted dehydrogenation. Harsher treatments or previous extraction steps could be an interesting avenue to address this issue.

In conclusion, the work presents an exciting step towards the selective chemical deconstruction of PE back to monomers at relatively mild conditions. Further research should focus on developing more potent and stable catalysts, improving the process design and dealing with more realistic plastic waste sources. The study will serve as inspiration for the polymer and catalysis communities to further develop mild and selective depolymerization processes.

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Conflict of Interest

The authors declare no conflict of interest.

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