

# Chemical Open-Loop Recycling of Polyethylene

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*The scientific challenge currently receiving much attention is the catalytic conversion of non-biodegradable polymers into versatile chemical platform molecules. As a model of a chemical upcycling process, we have developed a homogeneous catalytic system to break down persistent polyethylene waste into valuable chemical intermediates that could ultimately be used to produce important chemical products, including environmentally friendly, biodegradable plastics. In the first step, a smart pyrolysis of polyolefin waste yields oils, containing long-chain olefins as the major components. Then, for the next transformation step, tailored BICAAC-Ru olefin metathesis catalysts were used in combination with an alkene isomerization catalyst (RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>) for the transformation of the pyrolysis oil to propylene via isomerization metathesis (ISOMET) reaction in ethylene atmosphere. Eventually, translation of the highly efficient single-metal catalyst system enabled ISOMET reaction to a 900 mL reactor setup and repetitive batch experiments could prove the long-term stability of the catalyst system and the highest turn over number (TON = 3800) reported so far for propylene using polyethylene municipal waste feedstock. Propylene content in the gas phase achieved the 20 vol%. Ultimately, these results pave the way for the large-scale applicability of this process as a relevant demonstration of the combined application of adapted catalyst design and chemical engineering optimization with the aim of establishing a multi-dimensional circular economy concept in the chemical industry.*

## Introduction

Plastics are one of the most important achievements of the chemical industry, are an essential factor for our high standard of living and provide key materials for the transformation towards a carbon dioxide-neutral society. However, the advantages of the materials are also offset by problems in the demanding plastics management. Plastics, currently produced at a scale of 400 million tons per year and projected to reach a yearly production capacity of 1 billion tons by 2050,<sup>1,2</sup> lack sufficient end-of-life options and are thus accumulating in the environment.<sup>3</sup> Polyethylene (PE) and polypropylene (PP) are particularly challenging as they account for 45%<sup>2</sup> of global plastic production and are largely used as short-lived packaging materials<sup>4</sup> with limited recycling potential.<sup>5–8</sup> Currently, polyolefins are mainly recycled industrially *via* mechanical recycling processes, requiring high purity PE and PP streams. Nevertheless, in mechanical recycling, the product quality decreases with each recycling loop. This effect is attributed to the thermal and mechanical stress on the polymer during recycling, which can result in chain shorting. The decrease in quality is further facilitated by the presence of

different additives, such as flame retardants, pigments and plasticizers.<sup>8</sup> However, new chemical recycling technologies based on olefin metathesis reaction which can convert PE with ethylene to propylene have recently been proposed as an important alternative and could be demonstrated by Scott and Guironnet,<sup>9</sup> Hartwig<sup>10</sup> and in our laboratories.<sup>11,12</sup> These technologies offer the possibility to use polyolefin waste as a feedstock for the chemical industry. Moreover, the propylene product of this transformation is widely used in the petrochemical industry to provide essential chemicals and intermediates, e.g. polypropylene, propylene oxide, butanal, acrolein, acryl nitrile or isopropanol. Furthermore, propylene can also be used for the synthesis of recyclable and biodegradable polymers such as polylactic acid (PLA), polybutylene adipate terephthalate (PBAT) or polybutylene succinate (PBS). The metathesis-based conversion of PE to propylene, therefore, highlights the potential of the open-loop recycling approach, where a waste material can be utilized as a flexible and versatile feedstock. Essentially, it allows recovering the carbon atoms and synthesis effort which have been invested at the start of the product life cycle. This open-loop approach therefore forms the basis for building a multi-dimensional circular economy in the chemical industry (figure 1).

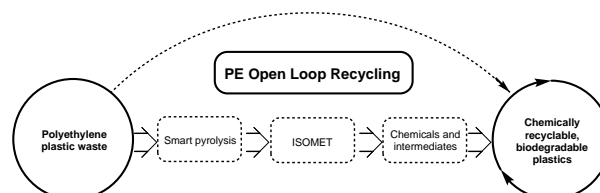
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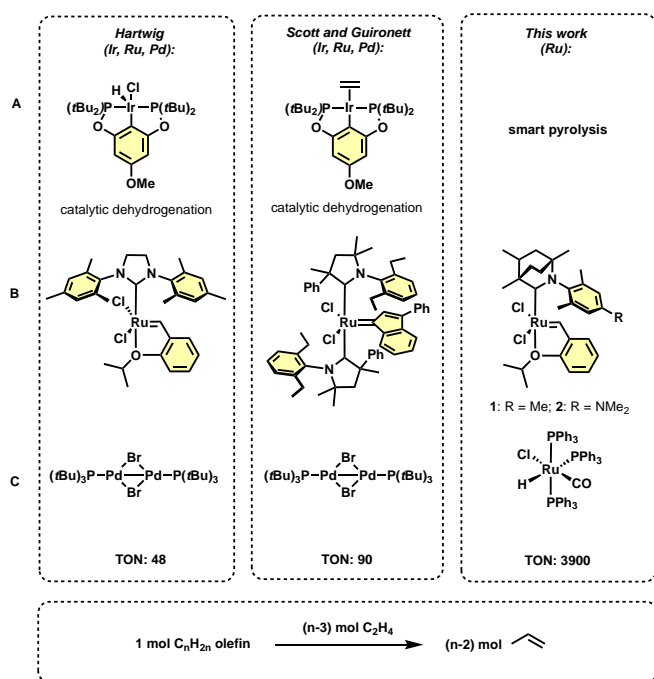
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**Figure 1.** Open-Loop Recycling: using PE-waste as feedstock to produce value-added molecules. A tentative example for open-loop concept contributing to the circular economy: by transforming polyethylene (PE) plastic waste to propylene, even biodegradable, chemically recyclable polymers could be produced.<sup>13</sup>



**Figure 2.** Polymer pretreatment (A) and isomerization metathesis (ISOMET; B: metathesis; C: double bond isomerization) catalyst systems for conversion of HDPE municipal plastic waste to propylene.

The studies by Scott and Guironnet<sup>9</sup> and Hartwig<sup>10</sup> highlighted already the feasibility of addressing PE valorisation through isomerization metathesis (ISOMET) after an initial dehydrogenation reaction (figure 2) using a ternary metal catalyst system (Ir, Ru and Pd). This work led us to extend the general concept by replacing the dehydrogenation step with a simple pyrolysis step to obtain olefin-rich pyrolysis oils, which are a novel suitable starting material for ISOMET reactions (figure 2 and S13). In contrast to dehydrogenation approaches, pyrolysis of plastic waste has already reached a relevant technology readiness level (TRL),<sup>14</sup> with a focus on the integration of pyrolysis products into conventional petrochemical refineries. In addition to all this, the use of a single-metal catalyst system has many advantages, both from an economic and environmental point of view, including much simpler metal recovery. Thus, the development of a pyrolysis process to yield olefin-rich pyrolysis oil mixtures from PE waste<sup>15–19</sup> for adaption to highly efficient single metal ISOMET catalyst systems enabled transformations represents an important next development.

Recently, the ISOMET reaction of long-chain olefins was demonstrated and using 1-octadecene as model substrate, our tandem catalytic system produced shorter-chain olefins with high efficiency, ultimately propylene. The performance of the ISOMET catalyst system is measured by the turn-over number (TON) based on the following equation:

$$TON = \frac{n(\text{propylene})}{n(\text{metathesis catalyst})}$$

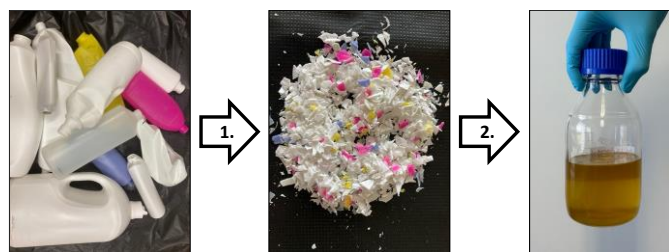
In these model reactions, already a TON of 55,000 could be reached in the conversion of 1-octadecene. This value can be clearly illustrated by the fact that an impressive 3.7 tons of

propylene could be produced from one kilogram of olefin metathesis catalyst and 1.4 tons of long-chain olefins.<sup>11</sup>

After the studies with 1-octadecene confirmed the original concept, we turned our attention here to the transfer of the ISOMET process to the pyrolysis oil of waste high-density polyethylene (HDPE). The key performance indicators for the applied sustainable overall process would require low catalyst loading, moderate ethylene pressure at low temperature.<sup>13,20</sup> Herein, it is envisaged to convert the complex olefin mixture in the HDPE pyrolysis oil with the tailored and robust BICAAC-ruthenium metathesis catalysts **1** and **2** (figure 2). In addition, the applicability of the improved approach should be demonstrated by transferring the reaction from the laboratory scale to the liter scale.

## Results and discussion

Pyrolysis is the decomposition of organic substances under the influence of heat and in the exclusion of oxygen. Depending on the process conditions, pyrolysis typically produces a mixture of molecules in the form of liquid or wax as the main product, which can be refined into chemicals or fuels in the existing petrochemical infrastructure. Pyrolysis is already a mature technology and commercial biomass, and plastics-based plants are in operation. Although pyrolysis is a relatively simple process, it can be used to treat various types of plastic waste. By using PE as a feedstock, the effectiveness of the ISOMET reaction can now be optimized based on controlling the amount of olefins and by-products produced.<sup>21</sup> Consequently, the developed smart pyrolysis of polyethylene at temperatures below 500 °C results in a mixture of saturated and unsaturated hydrocarbons. In detail, the pyrolysis of HDPE plastics was carried out in a 1250 cm<sup>3</sup>, electrically heated, stainless-steel batch reactor in the temperature range of 420–450 °C in nitrogen gas stream for 3 hours, yielding pyrolysis oil and small amounts of gaseous and solid by-products. The condensed hydrocarbons were separated from gaseous products in a phase separator. To demonstrate the applicability of the ISOMET reaction on pyrolysis oils from the smart pyrolysis, two qualities of pyrolysis oils were produced, namely, virgin crude and communal crude. Virgin crude was obtained by pyrolysis of virgin HDPE granules, while communal crude was obtained by pyrolysis of sorted and washed municipal HDPE waste (figure 3). The analysis of pyrolysis product mixtures showed that in the pyrolysis of virgin HDPE granules, 90 wt% of HDPE was transformed into pyrolysis oil, while the remaining HDPE was converted to gaseous products (9 wt%) and solid products (1 wt%). When subjecting the sorted and washed municipal HDPE waste to the pyrolysis, the share of solid residue increased to 25 wt%, while 62 wt% of the HDPE was recovered as pyrolysis oil with the remaining 13 wt% being collected as gaseous products. This shift in the product distribution is attributed to the more heterogeneous composition of municipal plastics (e.g. colorant and other additive contaminations).



**Figure 3.** Conversion of assorted communal HDPE plastic waste to pyrolysis oil. Arrow (1) represents plastic shredding; arrow (2) stands for smart pyrolysis (See ESI).

Each of the liquid fractions, from virgin and municipal HDPE waste, were further fractionated at 100 °C and reduced pressure (0.2 mbar) yielding the respective light (up to C10) (virgin: 32 wt%; municipal: 37 wt%) and heavy (m.p. 25–30 °C, >= C11, see figures S3–5, virgin: 68 wt%; municipal: 63 wt%) fractions. GC-MS analysis of the hydrocarbon mixture showed that each homolog structure consists of three signals: the corresponding alkane, alkene, and diene species. (figure S3, alkane, and alkene species are the major, dienes are the minor components). In the recent case, based on the quantitative GC-MS analysis of the pyrolysis oils 55 wt% alkanes, 40 wt% alkenes and 5 wt% dienes were observed (see SI for details). According to the NMR analysis, the mixture contains mainly terminal olefins (figure S6). Considering the gas phase composition, GC analysis revealed 26 vol% propylene and 12 vol% ethylene content. The rest involves saturated C1 – C5 hydrocarbons (figure S2).

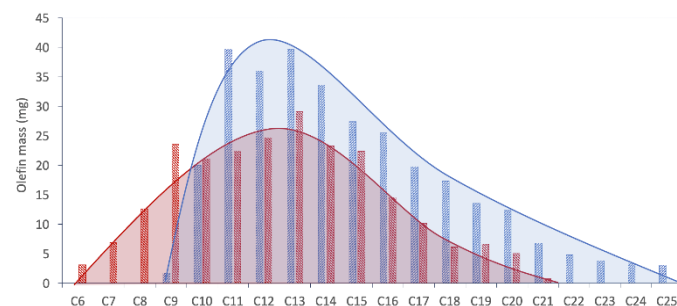
The subsequent laboratory reactor tests for the envisaged ISOMET reaction of HDPE pyrolysis oils with the dual catalyst system **2** (for metathesis) and **RuH** (for double bond isomerization, figure 2) were then carried out using a Fisher-Porter bottle at an ethylene pressure of 10 bar and a reaction temperature of 75 °C. In the first experiments with pyrolysis oil from pure HDPE (virgin crude), it was found that the propylene yield was relatively low and only a turn-over number (TON) of 800 could be observed (entry 1, table 1). When using only the virgin heavy fraction from the pyrolysis oil, the ISOMET reaction with catalyst **2** showed an increased TON of 4800 after 3 hours and 6800 after 24 hours (entry 2, table 1), while with the separated light fraction only a TON of 500 could be obtained (entry 3, table 1). These results confirm that the decreased TON of the virgin crude can be majorly attributed to low boiling compounds which inhibit catalysis. Following the investigations of pyrolysis oil from virgin PE, the reaction was performed with the communal crude pyrolysis oil, yielding a TON of 350. Albeit the comparably low TON, this result confirms the applicability of the catalyst system for additive and impurities containing materials (entry 4, table 1). Analogously to the reactions with virgin HDPE, ISOMET reactions were performed with the separated communal light fraction, and communal heavy fraction. The ISOMET reaction of the communal heavy showed an increased TON of 900 after 3 hours and after 24 hours a TON of 1400 (entry 5, table 1). When using the communal light fraction, a decreased propylene yield corresponding to a TON of 250 for propylene was observed (entry 6, table 1).

**Table 1.** ISOMET of HDPE pyrolysis oil. Setup: 3.2 g HDPE pyrolysis oil in 3 mL toluene, metathesis catalyst **2** (0.5 mg, 0.81 μmol), isomerization catalyst **RuH** (20 mg, 21 μmol),  $t = 75\text{ }^{\circ}\text{C}$ ,  $p_{\text{ethylene}} = 10\text{ bar}$  (99.9% purity).  $\text{TON} = n(\text{propylene produced}) / n(\text{catalyst } 2)$ .

Entry	HDPE pyrolysis oil feed	TON at 3 h	TON at 24 h
1	Virgin crude	800	ND
2	Virgin heavy	4800	6800
3	Virgin light	500	ND
4	Communal crude	350	ND
5*	Communal heavy	900	1400
6	Communal light	250	ND
7*	Communal heavy (filtered)	1900	3900

\*2.5 mg (4.1 μmol) catalyst **2** and 100 mg (105 μmol) catalyst **RuH**, 3.2 g HDPE pyrolysis oil in 5.5 mL toluene. (ND: no data)

Subsequently, the communal heavy fraction was filtered through an alumina plug. Impressively, this purification resulted in a significant increase in propylene with TONs of 1900 after 3 hours and 3900 after 24 hours of reaction time (entry 7, table 1). This correlates to a gas phase composition of 11 vol% propylene after 3 hours of reaction time and over 23 vol% after 24 hours. The concentration of propylene in the gas phase of 23 vol% is indicative of reaching the chemical equilibrium of the reaction in a closed reactor system. The investigation of the reaction mixture and the mass balance at approximately 30% olefin conversion revealed a significant shift in the chain length distribution of the olefins (figure 4). Prominently, the C19 – C25 olefins were converted to short-chain olefins and the C8 – C10 olefins - which were not present in the pyrolysis oil before the reaction - could be detected. The difference between the blue and red curves turned predominantly to propylene (figure 4) which has been indicated by quantitative GC-FID (gas phase) and GC-MS (liquid phase) analysis. These results confirm that the applied catalyst system does not have a kinetic preference for the degradation of a particular olefin component but can convert all olefins in the mixture. It has also been demonstrated that ISOMET reaction starting from 750 mg of pyrolysis oil (1 mL) containing 300 mg of long chain olefins gave 510 mg of propylene and 110 mg of butene, corresponding to 87% yield (considering the long-chain C15 olefins as a statistical mean component of the olefin content of the pyrolysis oil, table S5).



**Figure 4.** Analysis of communal heavy pyrolysis oil at appr. 30% olefin conversion. Composition before (blue) and after (red) the ISOMET reaction. ISOMET conditions:  $n(2) = 4.1\text{ }\mu\text{mol}$ ,  $n(\text{RuH}) = 105\text{ }\mu\text{mol}$ ,  $m(\text{pyrolysis oil}) = 0.8\text{ g}$ ,  $V(\text{toluene}) = 5.5\text{ mL}$ ,  $p_{\text{ethylene}} = 10\text{ bar}$ ,  $T = 75\text{ }^{\circ}\text{C}$ ,  $t = 24\text{ h}$ . (See ESI).

The analysis of the remaining liquid fraction indicated only traces of remaining olefin in addition to the presence of saturated hydrocarbons (figure S9).

Fogg et al. have demonstrated possible intrinsic deactivation pathways of NHC and CAAC-based ruthenium metathesis catalyst,<sup>22,23</sup> and thus a systematic study on the catalyst activity in the presence of potential plastic waste contaminants was carried out. Therefore, alcohols, thiols, amines, and dienes were added to reactions with the model substrate 1-octadecene (table 2). Without any additives, a TON of 13.400 for propylene could be obtained (entry 1, table 2) within 3 hours. The addition of 50 ppm 1-dodecanol had an inhibitory effect which resulted in a decreased TON for propylene of 9200 (entry 2, table 2). The presence of ethanethiol limited the TON of propylene further to 4000 (entry 3, table 2). Interestingly, the primary amine, 1-dodecylamine, had a significant inhibitory effect and the TON of propylene decreased from 13.400 to 2700 (entry 4, table 2). However, the addition of both hydrochloric acid and amines showed less deactivation (TON = 6000, entry 5, table 2), suggesting that the amine impurities can possibly be mitigated by protonation of the amines while maintaining the catalyst activity. In addition, the influence of dienes on the catalyst activity was investigated. It was found that the addition of 1,5-hexadiene and 1,7-octadiene resulted in a decreased TON of 5700 and 6000 (entries 6 and 7, table 2). Further systematic studies showed that increasing the 1,7-octadiene impurity concentration resulted in gradual deactivation of the catalyst (figure S7, table S4). This effect may be explained by the *in-situ* formation of conjugated species, which can inhibit the catalyst activity, resulting in faster decomposition and thus shortening the catalyst lifetime.

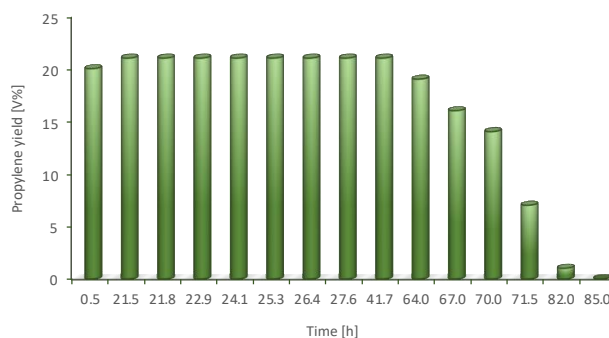
To investigate the robustness reaction, the key performance indicators regarding TRL increase, the setup was changed from Fisher-Porter bottles to high-pressure steel reactors, while simultaneously increasing the reactor size up to 900 mL reactors, which corresponds to the use of 110 mL of pyrolysis oil. To ensure a high ethylene concentration in the liquid phase, special gas-intake stirrers were used (see Fig. S12). Analytics were performed by an on-line GC-FID (see ESI for detailed description).

The upscaled reactions were performed with both, 1-octadecene and pyrolysis oil, for catalyst **1** and **RuH** (see ESI). Residence times, ethylene pressure and reaction temperatures had to be adjusted to account for the new reactor geometry. Having established consistent reaction conditions for the 900 mL reactor, repetitive batch reactions of pyrolysis oil were carried out using metathesis catalyst **2** and 99.95% (3.5) pure ethylene. After each measurement by GC, the gas phase was exchanged to ethylene in operation.

**Table 2.** Investigation of ISOMET of 1-octadecene in the presence of different contaminants. Setup:  $t = 75\text{ }^{\circ}\text{C}$ ; toluene; [1-octadecene] = 1.95 M; [2] = 10 ppm; [RuH] = 200 ppm;  $p_{\text{ethylene}} = 10\text{ bar}$ ; 3 h; contaminants = 50 ppm.

Entry	Contaminants	TON at 3 h
1	none (blank)	13400
2	1-dodecanol	9200
3	ethanethiol	4000
4	1-dodecylamine	2700
5	1-dodecylamine · HCl	6000
6	1,5-hexadiene	5700
7	1,7-octadiene	6000

Impressively, the reaction reaches a near-equilibrium concentration of propylene in the gas phase after only 0.5 h. For comparison, to reach similar concentrations the reactions in the Fisher-Porter bottles had to be run for 24h. Within the first 0.5 h, the analyzed gas phase contained 20 vol% propylene, achieving a TON of 350 for propylene. In the further course of the ISOMET reaction, constant propylene volume fractions of 21 vol% were obtained in the gas phase achieving TONs of around 370, demonstrating the long-term stability and activity of the catalytic system in combination with the heavy fraction from the communal PE pyrolysis oil (figure 5). After a reaction time of 64 hours, a decrease in the propylene yield was observed indicating catalyst deactivation (TON: 9 vs. 370, figure 5) and after 85 hours of operation, propylene could no longer be detected in the gas phase. Finally, in the repetitive batch experiments with a 900 mL reactor setup, a total turnover number (TON) of 3800 could be achieved which is equal to the production of 17.6 g of propylene from 30 g of olefin in the pyrolysis oil. While the TON is comparable to the batch experiment in Fisher-Porter bottles, these experiments showcase the high catalyst lifetime in the communal pyrolysis oil. In addition, it was shown that the olefin portion of the pyrolysis oil can be completely converted into propylene by shifting the chemical equilibrium during repeated gas exchange across the reaction mixture.



**Figure 5.** Yield-time profile in the large-scale high-pressure reactor for the conversion of HDPE municipal plastic waste pyrolysis oil to propylene. In the presence of catalyst **2** for 85 h time-on-stream (vol%: propylene content of the gas phase). (See ESI chapter 3.7).



**Figure 6.** A Sankey diagram representing the total mass balances of the HDPE polymer pretreatment and ISOMET process. The complete olefin ISOMET conversion of the heavy fraction was demonstrated on municipal HDPE plastic waste pyrolysis oil. The remaining alkanes can be further utilized by pyrolysis or catalytic dehydrogenation.

## Conclusions

Efficient conversion of PE waste to propylene using smart pyrolysis followed by a single-metal ruthenium-catalyzed ISOMET reaction was demonstrated. This process can pave the way for the introduction of a multi-dimensional circular economy, where instead of only closing the PE material cycle, cycles with linkages to different production networks are possible. This open-loop strategy not only allows the consumption of fossil oils to be reduced, but also offers the possibility of providing an entirely new feedstock platform from which chemical conversion processes can begin. The conversion of municipal PE waste was demonstrated in detail, which underlines the stability of the process against impurities and additives. Although reduced catalyst activities were observed when switching from virgin pyrolysis oil to the communal pyrolysis oil, larger-scale reactions demonstrate exceptional stability of the homogeneous catalyst system. Ultimately, one can imagine that 75 g of propylene can be produced from 100 g of PE waste and 45 g of (preferably bio-based) ethylene (figure 6). The remaining alkane fraction can be fed into established conversion processes such as steam cracking or FCC. With the tailored setup used, a TON of 3900 could be achieved (entry 7, table 1), scaling to a 900 mL reactor and repeated batch experiments showed the long-term stability of the catalyst system with a TTON of 3800 after 82 hours of operation. This is the highest TON reported for municipal polyethylene waste ISOMET systems so far. Based on these results, work is currently underway to develop a continuous flow system to pave the way for large-scale applicability of the system.

## Author Contributions

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## Conflicts of interest

There are no conflicts to declare.

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## References

- 1 R. Geyer, J. R. Jambeck and K. L. Law, *Sci Adv*, 2017, **3**, 25–29.
- 2 Plastics – the fast Facts 2023, <https://plasticseurope.org/de/knowledge-%0Ahub/plastics-the-fast-facts-2023/>.
- 3 A. Zeynep and G. Basak, *Environmental Pollution*, 2019, **254**, 113011.
- 4 R. Geyer, *Production, use, and fate of synthetic polymers*, Elsevier Inc., 2020.
- 5 L. D. Ellis, N. A. Rorrer, K. P. Sullivan, M. Otto, J. E. McGeehan, Y. Román-Leshkov, N. Wierckx and G. T. Beckham, *Nat Catal*, 2021, **4**, 539–556.
- 6 M. Baur, F. Lin, T. O. Morgen, L. Odenwald and S. Mecking, *Science (1979)*, 2021, **374**, 604–607.
- 7 A. Chamas, H. Moon, J. Zheng, Y. Qiu, T. Tabassum, J. H. Jang, M. Abu-Omar, S. L. Scott and S. Suh, *ACS Sustain Chem Eng*, 2020, **8**, 3494–3511.
- 8 A. H. Westlie, E. Y. X. Chen, C. M. Holland, S. S. Stahl, M. Doyle, S. R. Trenor and K. M. Knauer, *Macromol Rapid Commun*, 2022, **43**, 1–15.
- 9 N. M. Wang, G. Strong, V. DaSilva, L. Gao, R. Huacuja, I. A. Konstantinov, M. S. Rosen, A. J. Nett, S. Ewart, R. Geyer, S. L. Scott and D. Guironnet, *J Am Chem Soc*, 2022, **144**, 18526–18531.
- 10 R. J. Conk, S. Hanna, J. X. Shi, J. Yang, N. R. Ciccina, L. Qi, B. J. Bloomer, S. Heuvel, T. Wills, J. Su, A. T. Bell and J. F. Hartwig, *Science (1979)*, 2022, **377**, 1561–1566.
- 11 M. Nagyházi, Á. Lukács, G. Turczel, J. Hancsók, J. Valyon, A. Bényei, S. Kéki and R. Tuba, *Angewandte Chemie International Edition*, 2022, **61**, e2022044.
- 12 V. Farkas, D. Csókás, Á. Erdélyi, G. Turczel, A. Bényei, T. Nagy, S. Kéki, I. Pápai and R. Tuba, *Advanced Science*, 2024, **2400118**, 1–9.
- 13 V. Farkas, M. Nagyházi, P. T. Anastas, J. Klankermayer and R. Tuba, *ChemSusChem*, 2023, **16**, e202300553.
- 14 A. Maisels, A. Hiller and F. G. Simon, *ChemBioEng Reviews*, 2022, **9**, 541–555.
- 15 N. Miskolczi, A. Angyal, L. Bartha and I. Valkai, *Fuel Processing Technology*, 2009, **90**, 1032–1040.
- 16 D. Zhao, X. Wang, J. B. Miller and G. W. Huber, *ChemSusChem*, 2020, **13**, 1764–1774.
- 17 I. Ahmad, M. Ismail Khan, H. Khan, M. Ishaq, R. Tariq, K. Gul and W. Ahmad, *Int J Green Energy*, 2015, **12**, 663–671.
- 18 S. Kumar and R. K. Singh, *Journal of Petroleum Engineering*, 2013, **2013**, 1–7.
- 19 J. A. Onwudili, N. Insura and P. T. Williams, *J Anal Appl Pyrolysis*, 2009, **86**, 293–303.
- 20 A. H. Hoveyda and A. R. Zhugralin, *Nature*, 2007, **450**, 243–251.
- 21 N. Netsch, J. Vogt, F. Richter, G. Straczewski, G. Mannebach, V. Fraaije, S. Tavakkol, S. Mihan and D. Stapf, *Chem Ing Tech*, 2023, **95**, 1305–1313.
- 22 D. L. Nascimento and D. E. Fogg, *J Am Chem Soc*, 2019, **141**, 19236–19240.
- 23 D. L. Nascimento, M. Foscatto, G. Occhipinti, V. R. Jensen and D. E. Fogg, *J Am Chem Soc*, 2021, **143**, 11072–11079.