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COMMENTARY

The Innovation Materials

Circular polyethylene with low-density in-chain functionalities

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Plastics are integral to modern life, offering essential convenience and versatility due to their lightweight, durable, and cost-effective nature. As the most widely used plastic, polyethylene (PE) production is projected to reach 135 million metric tons by 2030, approximately one-third of the global plastic market volume. However, its production and consumption systems are unsustainable, as PE is primarily derived from petroleum-based chemicals, and over 90% of post-consumer PE is discarded as waste or incinerated for energy recovery (Figure 1A). To address this challenge, recycling chemicals from waste PE is crucial for a carbon-neutral future.

The most straightforward strategy is by breaking the inert C–C bonds on the backbone of PE. Successfully, detergent precursors, liquid fuels, and monomers for making polypropylene and polyesters are obtained from wasted PE.[1] Two apparent drawbacks go hand in hand with these methods: harsh degradation conditions and the inability to remake PE from recycled chemicals. Thus, PE mimics, prepared by installing chemically labile groups into PE chains without compromising their thermochemical performances, are viewed as a promising approach to facilitate chain scission during chemical recycling.[2] Ideally, PE mimics with the same chemical structure and physical properties can be remade from the recycled chemicals. Mecking and coworkers demonstrated such closed-loop chemical recycling behavior of PE-like plastics with hydrolytically degradable ester or carbonate groups in 2021.[3] These polymers were originally made from 18-carbon diacids, and the degraded product needs to be recrystallized to recycle the chemicals (Figure 1B). Considering the raw material availability and purification-related costs, there still exist tremendous challenges ahead.

Now, writing in *Nature Sustainability*, Jian and coworkers have developed degradable PE (*d*PE) using commodity raw materials, achieving significantly reduced and tunable ratios of ester groups on the polymer chain.[4] On one hand, the low density of ester groups (1% relative to the repeating ethylene units) ensures excellent chain packing in *d*PE-1% at the atom level, which is a crucial factor governing its application properties, such as melting temperature and low water absorption capacity. On the other hand, this density remains sufficiently high to cleave long polymer chains into fragmented chains with tailored molecular weights. As the ester group density increases (from 1% to 7%), shorter chains are obtained after degradation. Notably, through a conventional repolycondensation process, these uniform short fragments can be reconnected together to form PE-like plastics with performance metrics consistent with the parent polymer, thereby closing the loop of the polymer-short fragments-polymer cycle.

Metathesis copolymerization has been utilized to prepare degradable PE;[5] however, it remains challenging for the recycled materials to exhibit mechanical properties comparable to virgin polymers. Here in Jian's work, a well-defined 16-membered unsaturated lactone comonomer, Ester-16, was key to achieving the above-mentioned performances of *d*PE (Figure 1C). The pivotal structure of Ester-16 can be featured by two aspects. First, it is selectively prepared from the ring-closure reaction of an ester-containing diene precursor and can be readily obtained with yields up to 90%. Second, the energy required to open the ring structure of Ester-16 is theoretically calculated to be close to that of opening an all-carbon unsaturated ring monomer, cyclooctene (COE). Consequently, COE and Ester-16 can be copolymerized into polymer chains at similar rates, and the breakable ester group in Ester-16 is evenly distributed along the carbon backbone. The chain length between ester groups depends on the feeding ratio of COE and Ester-16. For example, when the feeding ratio of COE:Ester-16 is maintained at 20:1 or 10:1, there will be, on average, 80 carbon atoms or 40 carbon atoms from COE between two ester groups in *d*PE, respectively. Since a ring-opening metathesis polymerization process is employed, which is a well-established method for producing high-molecular-weight polymers, *d*PE with a number-average molecular weight (M_n) up to 140,000 Da was obtained, falling within the range of traditional high-density polyethylene (HDPE, 50,000–250,000 Da). Due to the low density of ester groups and high molecular weight, these PE mimics exhibit a similar crystalline structure, high melting point (T_m), good thermal stability,

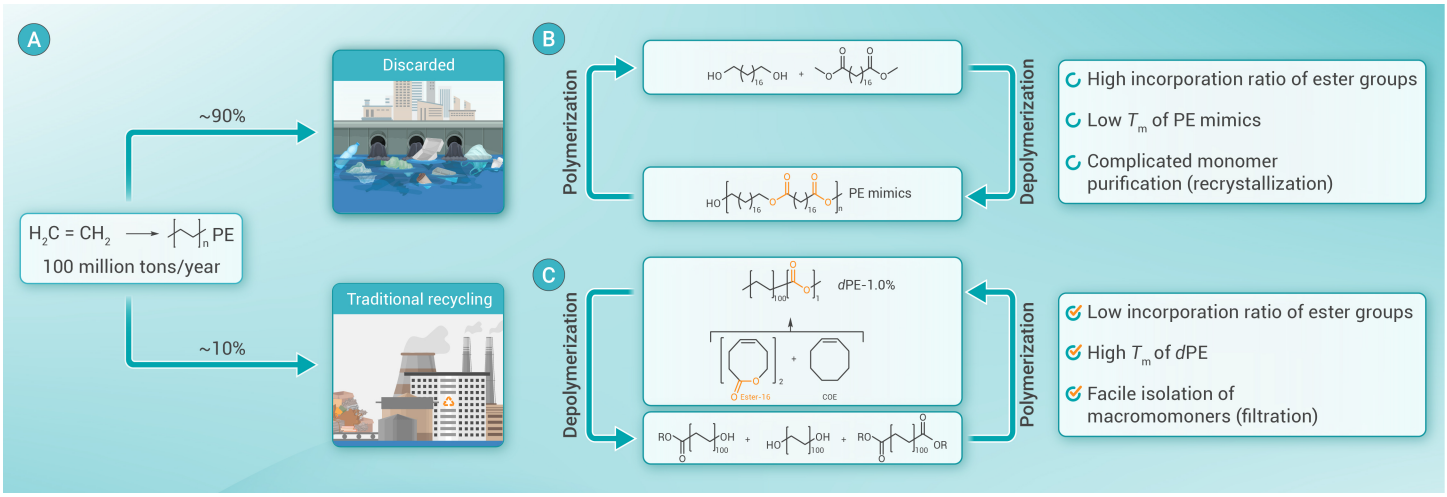

Figure 1. Different approaches for recycling PE (A) Traditional recycling of PE. (B) Chemical recycling of PE mimics enabled by polycondensation of diol with diacid developed by Mecking.[3] (C) Chemical recycling of PE-type polymers enabled by copolymerization of Ester-16 with COE with adjustable in-chain ester group density developed by Jian.[4]

and mechanical strength comparable to HDPE.

How would the low-density ester groups affect the post-usage recycling of *d*PE? These polymers can be completely degraded by methanol at 120°C when catalyzed by a base, such as potassium hydroxide. Short chains with M_n of 5,800 Da were obtained from *d*PE-1.0% (M_n=140,900 Da, T_m=130°C) after alcoholysis. The degradation products were isolated via simple filtration

from methanol following acidification with hydrochloric acid, eliminating the need for labor-intensive recrystallization or distillation steps that are typically required when dealing with small-molecule degradation products.[3] This degradation and recycling process demonstrated selectivity even in the presence of mixed commercial HDPE and isotactic polypropylene. Moreover, the recycled products contain equimolar amounts of hydroxyl (-OH) and carboxyl/ester (-COOH/COOMe) terminal functionalities, enabling them to act as AB-type macromonomers capable of self-polycondensation. This eliminates the need for additional monomers to balance stoichiometric ratios between functional groups. Through direct polymerization of the recycled macromonomer, *d*PE-1% was regenerated with an M_n of 172,400 Da and a slightly elevated T_m of 133°C. A second degradation-repolymerization cycle further confirmed the robustness of this system, yielding macromonomers with M_n = 5,700 Da and *d*PE-1% with T_m =133°C and M_n = 177,900 Da. These results underscore the exceptional closed-loop recyclability of such PE mimics with low in-chain ester group densities.

In summary, Jian and colleagues have developed an efficient strategy to create PE mimics featuring low-density (from 1% to 7%), evenly distributed ester groups along the polymer backbone. The spacing between these anchored ester groups can be easily tuned. This innovative structural design also simplifies the purification of degradation products, which can be thermally repolymerized to regenerate similar polymers without requiring additional monomers. Currently, global PE recycling rates remain dismal (~10%), with mechanical recycling dominating despite its energy-intensive nature and tendency to degrade material properties. In contrast, the chemical recycling approach presented here achieves 100% recovery efficiency while preserving material performance. Given the enormous scale of the PE market (100 million tons annually), this method offers compelling advantages for sustainable, iterative product life cycles. However, challenges remain. The strategy relies heavily on the synthesis and polymerization of the 16-membered unsaturated lactone monomer (Ester-16), both of which require Grubbs catalyst. Additionally, Ester-16 was prepared under diluted conditions (25 mM), potentially limiting production feasibility due to cost constraints for the first-generation *d*PE. Future endeavors on this macromonomer-polymer-macromonomer closed-loop system should prioritize three critical research directions: (1) establishing more cost-effective synthetic pathways, (2) exploring alternative chemical approaches, and (3) performing comprehensive life-cycle assessments coupled with detailed techno-economic analyses. These concerted efforts are essential for transitioning this promising technology from lab-scale validation to industrial-scale impact.

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DECLARATION OF INTERESTS

The authors declare no competing interests.