

New Uses for Recycled Carbon: Converting Waste Polyethylene into Alkylaromatics

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Polyethylene is the world's most widely used and produced polymer, highly valued for its lightness and strength. It is a key component of countless everyday items, such as plastic bags, bottles, caps, lids, pipes, containers, as well as many that are lesser-known, such as wire and cable insulation, woven fabrics and yarns, and wear-resistant artificial hip and knee joints. Although polyethylene itself is not directly harmful, being rather inert and essentially non-toxic, it makes up a significant portion of human-generated litter and environmental pollution; furthermore, the original source for its production is largely ethylene obtained from energy-intensive fossil fuel processing, which also represents a major environmental issue.

"The synthetic polymer industry is nearly 150 years old, but mass production really started to take off about 60 years ago and has been growing exponentially ever since," said Professor Susannah Scott, from the University of California, Santa Barbara (USA). "Polymer chemists learned how to tailor material properties by modulating both the molecular-level microstructure and the macromolecular entanglements using just carbon and hydrogen (and the occasional heteroatom), creating an industry which is now one of the largest non-energy uses for fossil carbon."

Professor Scott explained that the widespread adoption of plastic, driven by its low cost of production and robustness,¹ has led to increasingly visible pollution of the natural environment. Only a small fraction of used plastic is destined for mechanical recycling into polymer-based products, due to challenges in recovery and cleaning and degradation of properties during reprocessing. In some countries, incineration keeps most plastic out of landfills, but the process recovers far less energy than was invested in making the plastics. Conventional routes to feedstock recycling target monomers which can be repolymerized. "This is thermodynamically feasible for condensation polymers but not for addition polymers, of which the polyolefins such as polyethylene and polypropylene constitute the majority of plastic waste," said Professor Scott. "Alternative approaches involving hydrogenolysis can convert polymers into smaller molecules at lower temperatures due to the strong exothermicity of the reaction,² but require a relatively expensive co-reactant (H₂) and generate low-value paraffins as products. Such reactions may not provide

the necessary economic driving force to motivate polyolefin recycling, since the products can be obtained more cheaply (and potentially with a smaller environmental footprint) in alternative ways."

At the onset of this project, Professor Scott's group was inspired by a report on the depolymerization of polyethylene in which the homogeneous Ir-catalyzed dehydrogenation of polyethylene and *n*-hexane was coupled with Re-catalyzed olefin metathesis at 175 °C.³ Professor Scott said: "We initially attempted to conduct a solvent-free analogue of this reaction using two heterogeneous catalysts (Pt/Al₂O₃ and ReOx/Al₂O₃) and a low-molecular-weight polyethylene. It proceeded smoothly at 280 °C over the course of 24 hours to generate a hydrocarbon liquid with much-reduced molecular weight. However, a control reaction involving only the dehydrogenation catalyst revealed that the metathesis catalyst is not required. Indeed, depolymerization over Pt/Al₂O₃ in the absence of solvent gave a similar liquid. However, the orange color suggested the presence of polyaromatic chromophores. Further spectroscopic analysis by field desorption mass spectrometry revealed that alkylbenzenes are major products, with smaller amounts of higher polyaromatic hydrocarbons that contribute the visible color."

Since the formation of alkylaromatics is strongly endothermic at moderate reaction temperatures, the key to their formation is the coupling of aromatization with hydrogenolysis, which provides an internal source of energy. "The tandem reaction therefore benefits from having a macromolecular carbon source; much shorter hydrocarbon chains such as those found in crude oil cannot engage in the necessary reaction balancing," explained Professor Scott. She continued: "Control experiments with C₃₀H₆₂ failed to produce significant amounts of alkylaromatics, presumably because the shorter hydrocarbon chains are not an effective H₂ sink."

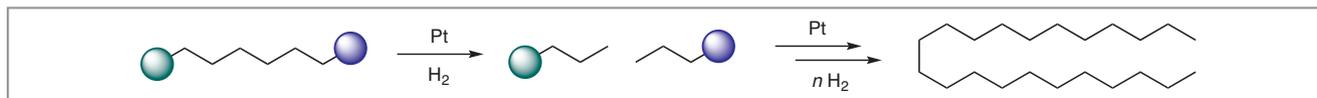
Professor Scott noted: "The aromatic fraction is predominantly dialkylbenzenes, which can be sulfonated to form anionic surfactants. These materials resemble the linear alkylbenzene sulfonates, which are biodegradable surfactants manufactured from fossil fuels."

"Future work will involve increasing the catalytic activity, increasing the alkylaromatic yield, and tuning the product distribution to favor particular molecular weights," said Pro-

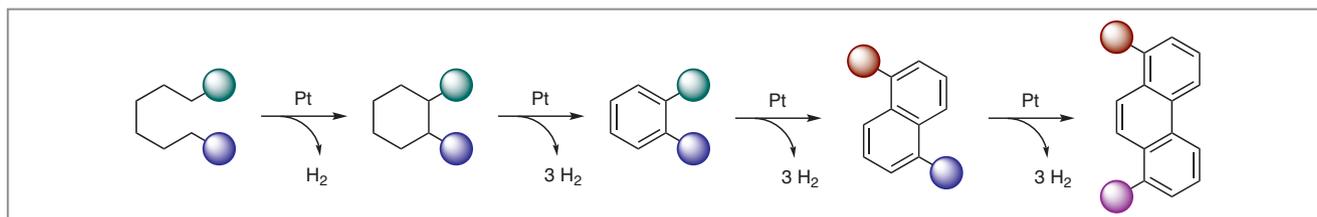
fessor Scott, who concluded: "For industrial application, the tolerance of the catalyst to impurities in post-consumer plas-

tic waste must be optimized, and the ability to conduct the reaction in a continuous fashion must be developed."

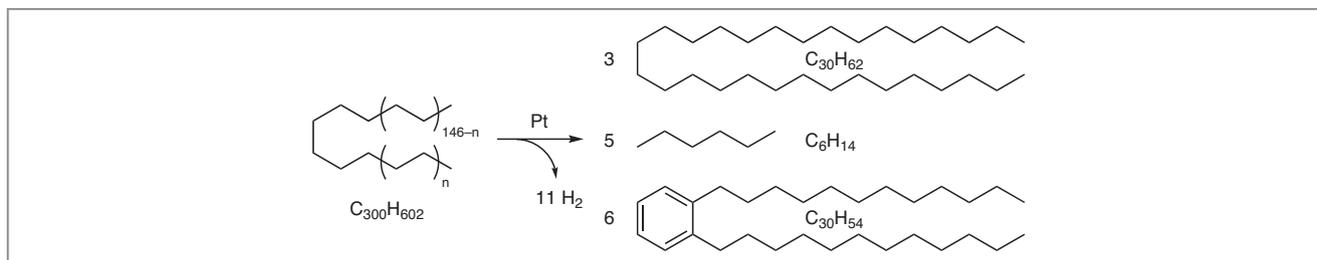
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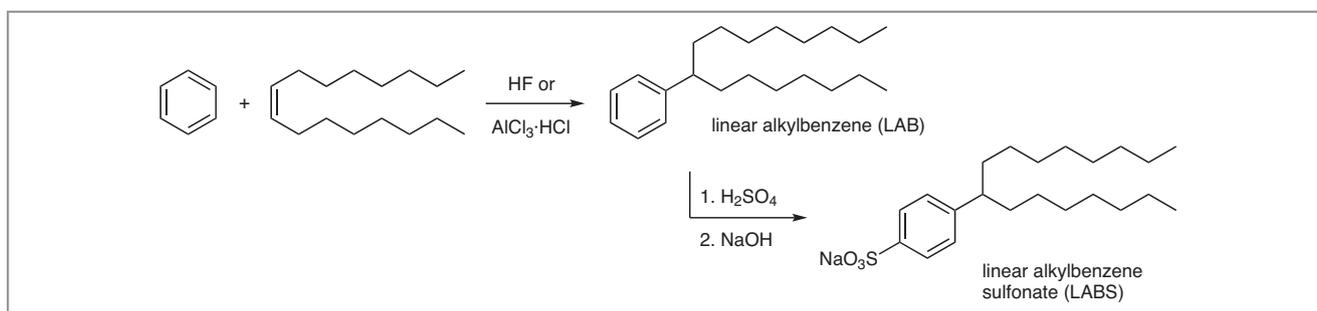
Scheme 1 Exothermic



Scheme 2 Endothermic



Scheme 3 Tandem hydrogenolysis/aromatization



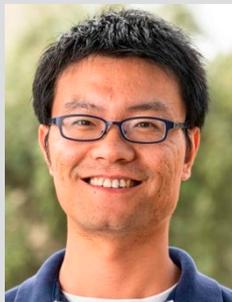
Scheme 4 Conventional manufacturing of alkylbenzene sulfonates

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