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Preview

Tandem triumphs in PVC upcycling

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SUMMARY

The current consequences of poly(vinyl chloride) (PVC) waste are bleak and far-reaching, and it is incompatible with traditional recycling processes. In recent issues of *J. Mater. Chem. A* and *Nature Chemistry*, Fieser and McNeil, respectively, present complementary approaches to upcycle PVC waste based on tandem catalysis.

MAIN TEXT

Since their large-scale manufacture became widespread after World War II, plastics have become an essential part of modern life.[1] The low cost, diversity, and durability that led to such ubiquitous usage have resulted in a global accumulation of waste material. A greener economy demands better options for recycling these post-consumer contents. In particular, poly(vinyl chloride) (PVC) is a major concern because it is widely used yet rarely recycled.

The pervasiveness of PVC is due in part to its versatility. PVC is inexpensive, moisture- and corrosion-resistant, and provides excellent thermal and electrical insulation. When blended with certain fillers and stabilizers, the polymer has increased rigidity, making it ideal for applications in construction. To obtain flexible PVC for applications including IV bags or shower curtains, plasticizers (most commonly phthalates) are added.[2] These additives, however, further complicate end-of-life processing. Mechanical recycling requires proper isolation of PVC in waste streams to avoid cross-contamination, which is difficult and expensive to implement. At elevated temperatures, PVC forms dangerous molecules like hydrochloric acid and dioxins. Therefore, melt processing and pyrolysis are not only bad for the environment but also lead to the corrosion of plant reactors. These problems culminate in a recycling rate of less than 1% in the United States, despite being produced at volumes only exceeded by polyolefins.[3] Furthermore, PVC is not easily contained in landfills, as leakage of microplastics and plasticizers has negative environmental and health effects.[4] Potential solutions involve dechlorinating PVC prior to entering general waste management, but this method has proven very energy-intensive and inefficient.[2] Fortunately, female scholars like Professors Megan Fieser (USC) and Anne McNeil (U. Michigan) are developing creative tandem catalytic approaches to both dechlorinate PVC waste and use it as a feedstock for higher-value products (Figure 1).

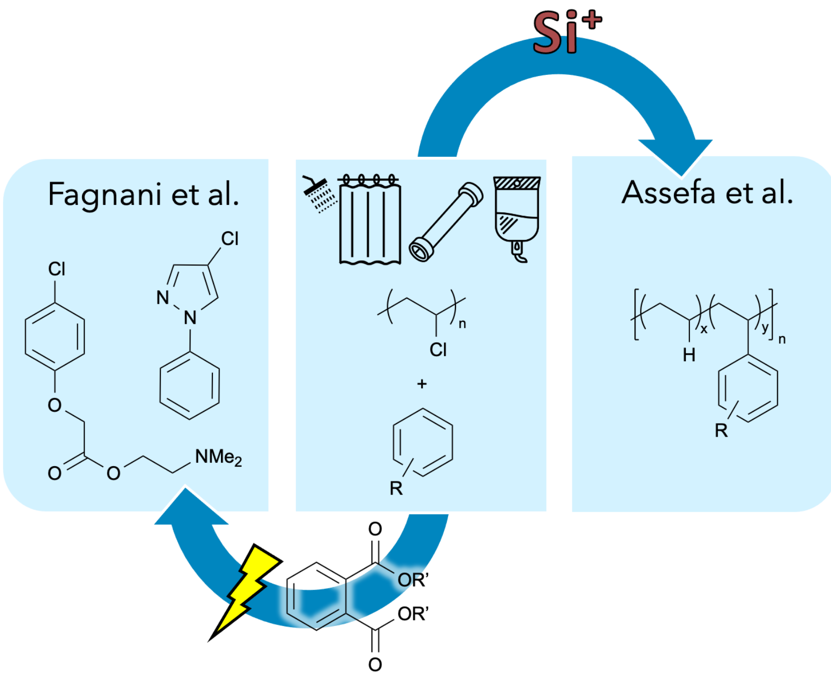

Figure 1. Two new methods for PVC upcycling via catalytic dechlorination, using electroreduction and hydrodechlorination. Shower Curtain by Rohan Gupta, IV Bag by hunotika, and pipe by Brickclay from thenounproject.com (CCBY3.0).

Decreasing the chlorine content of PVC reduces the hazards associated with its end-of-life processing or disposal, but is typically performed at elevated temperatures (>200 ºC), and the resulting complex mixture is at best pyrolyzed into smaller hydrocarbons.[2] Previous attempts to fully substitute the C–Cl bonds in PVC resulted in undesired side reactions. In a recent communication by Assefa et al. in *J. Mater. Chem. A*, PVC was successfully dechlorinated and converted into ethylene-styrene copolymers.[5] Rather than using base or elevated temperature, the authors found inspiration in a silylium cation-catalyzed hydrodehalogenation reaction developed by Ozerov to address greenhouse gases.[6] A trityl cation precatalyst abstracts hydride from stoichiometric Et_3SiH to generate a silylium cation, which rapidly abstracts chloride from PVC. The resulting secondary carbocation either abstracts hydride from additional silane or undergoes Friedel–Crafts alkylation with the aromatic solvent. Using benzene as the solvent at 110 ºC with just 0.5 mol% of the trityl precatalyst, the authors obtain 91% yield of a poly(ethylene-*co*-styrene) with 20 mol% benzene incorporation and a uniform molecular weight distribution. Complete removal of chlorine was confirmed by energy-dispersive X-ray spectroscopy, and side reactions such as crosslinking or cyclization were not observed. The structure of the copolymer could be varied by using different aromatic solvents, including toluene and *o*-, *m*-, and *p*-xylene. The resulting copolymers were amorphous, with glass transition temperatures (T_g) between 80 and 88 ºC, higher than typical ethylene-styrene copolymers.

Excitingly, the authors were able to perform the silylium-catalyzed tandem dechlorination/Friedel–Crafts alkylation using a commercial flexible PVC sample (lizard-shaped toys). Using 7.5 wt% of the trityl precatalyst relative to PVC, >95% dechlorination and 17% benzene incorporation was achieved within 1 hour at 110 ºC. This result suggests that the silylium catalyst tolerates the dyes, plasticizers, and other additives found in commercial PVC. Not only does this method efficiently dechlorinate PVC, it also produces ethylene-styrene copolymers that cannot be accessed by traditional Ziegler-Natta catalysis. The INDEX ethylene-styrene "interpolymers" produced by Dow are synthesized from petroleum feedstocks using their proprietary INSITE constrained metallocene catalysts, and have excellent properties for applications like foams.[7] Additional mechanical testing of the upcycled PVC copolymers will reveal whether these materials could be competitive substitutes. Furthermore, future technoeconomic and life cycle analyses could guide the choice of solvent, catalyst, or silane, potentially identifying more cost-effective or sustainable alternatives.

A complementary study published in *Nature Chemistry* by Fagnani et al. reimagines waste PVC as a source of chlorine that can be harvested for useful synthetic transformations.[8] The electrochemical process they develop is not just tolerant to additives in PVC but actually improved by the plasticizer. Again, a tandem process (paired electrolysis) is employed, consisting of PVC electroreduction to generate HCl and subsequent electrooxidation to promote arene chlorination. The precedent for the electroreduction comes from a publication by Shapoval et al. over thirty years ago,[9] but Fagnani et al. elucidate the role of the plasticizer as a redox mediator and pair this process with a synthetically useful chlorination reaction.

The authors initially use virgin PVC with a variety of molecular weights as the chlorine source and ethoxybenzene as the model arene substrate for chlorination. Their findings show that the common plasticizer di(2-ethylhexyl)phthalate (DEHP) can improve the yield of 1-chloro-4-ethoxybenzene under galvanostatic (constant-current) conditions, and is required to produce the product under potentiostatic (constant-voltage) conditions. Based on cyclic voltammetry, the authors conclude that DEHP undergoes semi-reversible reduction at the cathode. The reduced DEHP then transfers an electron to PVC, allowing the electroreduction of PVC to occur at smaller voltages. However, significant degradation of DEHP is also observed, compromising its efficiency as a catalyst. Following single-electron reduction of PVC, the authors hypothesize that loss of Cl^- generates macroradicals, which then undergo scission or coupling with other alkyl and aryl radicals produced during the paired-electrolysis process. The resulting polymer byproducts have ~8-23% less Cl content than the original polymer and contain alkene, aryl, and alkyl groups.

The Cl^- ions released from the PVC are then oxidized at the anode to form Cl_2 or ^-OCl, which chlorinate the arene. Electrochemical chlorination of various arenes and heteroarenes, including pharmaceutically-relevant substrates, was achieved using PVC as the chlorine source in 5–76% yield. Impressively, flexible PVC tubing was an effective chlorine source using this protocol, demonstrating that the plasticizers found in commercial products are sufficient to catalyze the electroreduction. The electrochemical method was also compatible with a simulated mixed plastic waste stream.

A notable feature of Fagnani et al's work is the application of life-cycle assessment (LCA) to examine the potential environmental impacts of the electrochemical process. Specifically, the authors compared global warming potential (GWP) for the electrosynthesis of 1-chloro-4-ethoxybenzene using HCl versus PVC waste as chlorine sources. Scenarios comparing landfilling vs. pyrolyzing the dechlorinated PVC were also compared. Even using a simplified assessment, the authors show significant decreases in GWP (56–71%) using PVC waste as a chlorine source, and they anticipate further benefits if pyrolysis technology is improved or if other environmental metrics are considered. These analyses underscore the importance of LCA in evaluating the potential impact of even nascent technologies for polymer upcycling. The authors also put forward a thought-provoking proposal to rethink plastic additives; in their work, DEHP's catalytic activity is fortuitous, but in the future additives with beneficial reactivity for end-of-life chemical recycling could be designed.

Tackling the plastic waste challenge will require a multitude of solutions from diverse perspectives. Professors Fieser and McNeil have both devised creative, forward-thinking approaches to upcycle one of the most challenging and hazardous forms of plastic waste using different forms of catalysis. Their innovations should serve as a clarion call for researchers in catalysis to embrace the challenges and opportunities in the field of plastic upcycling. Strategies that take advantage of catalysis, whether precisely-designed, highly active catalysts or adventitious catalysts that are already present as additives, will be necessary to decrease the energy input and improve the selectivity of chemical processes applied to polymer waste. We hope that the chemistry highlighted in these two articles aptly sum up how women in catalysis will continue to thrive: in tandem.

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DECLARATION OF INTERESTS

The authors declare no competing interests.

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