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Upcycling waste polyoxymethylene to value-added chemicals using reusable polymeric acid catalysts at ppm levels

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Waste polyoxymethylene (POM) plastic was upcycled using m-phenolsulfonic acid-formaldehyde resin, a polymeric heterogeneous catalyst, to afford multiple value-added chemicals, including solvents, insecticides, herbicides, and pillar[5]arenes using biomass-derived alcohols, amines or water as reactants. The acid catalyst exhibited stable and reliable performance at a 260 mol ppm S loading and remained active after five reuse cycles without any loss of catalytic efficiency. The upcycling process was effective even at a 40-gram scale. Under acid-catalyzed conditions, the POM moiety in carbon-fiber-reinforced polymers (CFRPs; 360 mg–5 g scale) was selectively depolymerized, yielding carbon fibers free of POM residues, as confirmed by solid-state NMR and SEM. This process also mitigates environmental concerns by converting microplastics into value-added chemicals. Additionally, microwave irradiation proved more effective (up to 99% upcycling) than conventional heating methods (73%). Life cycle assessment analysis results indicate that this upcycling process is sustainable and helps reduce environmental pollution.

Green foundation

1. Plastic pollution is escalating. Our new upcycling strategy for waste polyoxymethylene utilizes a reusable polymeric acid catalyst, overcoming previous methods that relied on non-recyclable catalysts and high energy demands.

2. We have successfully developed a method for upcycling waste polyoxymethylene using biomass-derived diols, alcohol, or water, with a recyclable polymeric acid catalyst at ppm levels and synthesize value-added chemicals. This methodology was effectively demonstrated at the 40 g scale and applied to microplastics and carbon fiber-reinforced polymers (CFRPs). Using microwave irradiation as an energy source enables selective, energy-efficient heating. A life-cycle assessment indicates that our approach is sustainable. This method contributes to SDG 7 (clean energy), SDG 12 (responsible consumption), and SDGs 14 and 15 (protecting life underwater and on land).

3. Further studies utilizing solar energy instead of grid electricity for upcycling waste polyoxymethylene will make the process greener.

Introduction

Plastics are ubiquitous in contemporary life owing mainly to their widespread availability and low cost: however, most plastic materials are non-degradable and non-reusable, resulting in significant plastic waste, which adversely affects both terrestrial and aquatic ecosystems and thus places a considerable burden on the environment.[1] Incinerating plastic is not a viable waste management solution because this process emits copious greenhouse gases.[2] The chemical upcycling of plastic waste has therefore attracted increasing attention.[3–19] Plastic upcycling aims to transform waste materials into value-added chemicals in accordance with the Sustainable Development Goals (SDGs), a global framework for environmental, social, and economic sustainability set up by the United Nations.

Polyoxymethylene (POM), also known as polyacetal and commonly referred to as engineered thermoplastic, is a versatile plastic used in various everyday items, including buckles, kitchen utensils, motor gears, joints, lighters, and coffee brewers.[20] It is known for its high mechanical strength, stiffness, and water-repellency. Hence, the demand for POM has increased, with the current global production capacity reaching approximately 1900 kilotons annually.[21] However, POM materials are difficult to recycle and exacerbate environmental pollution. POM can be treated using various methods

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such as mechanical recycling,[22] electrochemical depolymerization,[23,24] and pyrolysis;[25] however, mechanical recycling typically does not reconvert the polymeric plastic into monomers and thus downgrades the polymer, while pyrolysis aggravates greenhouse gas emissions. Although electrochemical depolymerization produces small molecules, the reaction is non-selective.[24] Electrochemical depolymerization also requires solvents and electrolytes and is therefore less atom-efficient. To address these issues, several studies have investigated the chemical upcycling of POM.[26–31] A method using formic acid and manganese catalysts produces methanol *via* POM upcycling; however, this method produces CO_2 and requires high reaction temperatures and long reaction times.[26] The synthesis of cyclic acetals such as 1,3-dioxane[27] or 1,3-dioxolane[28] from waste POM using $Bi(OTf)_3$ or 4-chlorobenzenesulfonic acid (4-$ClC_6H_4SO_3H$) catalysis has been achieved using diol derivatives (Fig. 1A). These cyclic acetals act as both solvents and reagents in the synthesis of 7- and 8-membered cyclic molecules;[32] they are also used in solid-state batteries[33] and for the storage of natural gas.[34] Despite yielding valuable cyclic acetals from waste POM, the reaction requires high catalyst loadings (0.2–5 mol%). In contrast, the alcoholysis of POM catalyzed by $Bi(OTf)_3$ affords valuable dialkoxymethanes; however, the process does not occur in water, necessitating the use of additional solvents.[29] The catalysts used in existing POM upcycling methods, including formic acid, $Bi(OTf)_3$, and 4-chlorobenzenesulfonic acid, are homogeneous and not reusable. Proton-exchanged montmorillonite-catalyzed POM upcycling has been reported.[30] However, this strategy requires a high catalyst loading (12.5 mg of catalyst for 50 mg of POM) and organic solvents. Similarly, a nano-H-beta-15-zeolite catalyzed POM upcycling has also been documented.[31] Unfortunately, this method also demands high catalyst loading (20 mg of catalyst for 30 mg of POM). Therefore, efficient processes are required to upcycle waste POM plastic with reusable catalysts to produce cyclic acetals and dialkoxymethanes under solvent-free conditions. Moreover, depolymerizing POM using water as a reactant offers several advantages, improving atom economy and enhancing sustainability.

A highly active, stable, and heterogeneous acid catalyst, *m*-phenolsulfonic acid-formaldehyde resin (PAFR II) was previously developed for continuous-flow esterification[35] and Ritter reactions.[36] The acid catalyst remained stable for more than two weeks of continuous use in both continuous-flow esterification and Ritter reactions, demonstrating excellent stability. Therefore, solid PAFR II was hypothesized to facilitate the upcycling of POM materials into value-added chemicals owing to its high stability and acidity. Additionally, using microwave irradiation as a heating source may enhance the efficiency of the reaction by selectively heating the heterogeneous catalyst.[37,38] The selective heating properties of microwaves can save electricity and thus contribute to achieving carbon neutrality by minimizing CO_2 emissions.[39] Thus, in this study, we developed a microwave-assisted reusable poly-
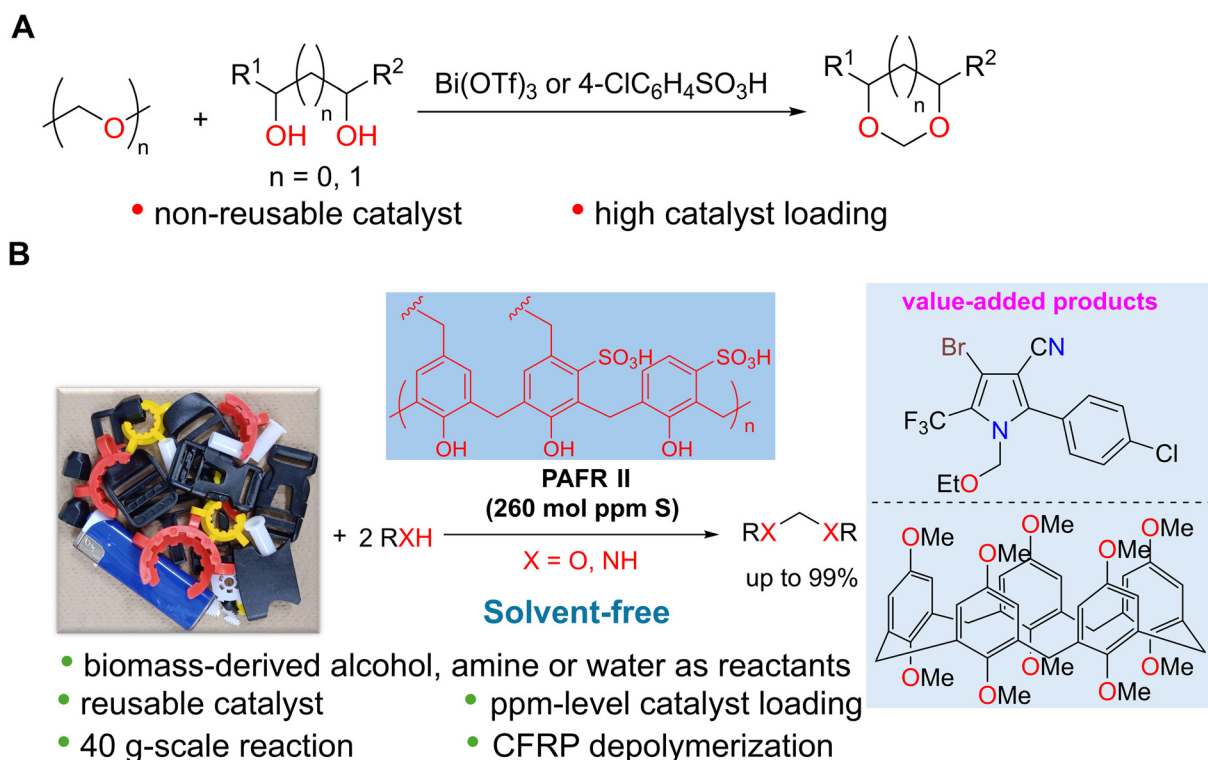

Fig. 1 Representative examples of POM upcycling using alcohol. (A) Upcycling of POM using homogeneous catalysts. (B) Upcycling of POM using a reusable polymeric acid catalyst (this study).

meric acid-catalyzed process for upcycling waste POM plastics (Fig. 1B). To the best of our knowledge, this is the first reported instance of waste plastic upcycling catalyzed by a reusable polymeric catalyst. This microwave-assisted plastic upcycling contributes to SDG 7 (clean and affordable energy *via* the use of microwaves as a heating source), SDG 12 (responsible consumption and production using biomass-derived alcohols, amines, and water), and SDGs 14 and 15 (life underwater and life on land *via* the decomposition of waste plastics and microplastics).

Results and discussion

Reaction development and optimization

Initial optimization of the reaction conditions was conducted using polyoxymethylene **1**. The reaction of **1** and 1,3-propanediol (**2a**) in the presence of the PAFR II catalyst (260 mol ppm S) was performed under microwave irradiation for 2 h, yielding 1,3-dioxane (**3a**) in 99% yield (Table 1, entry 1). Microwave heating was more effective than conventional methods, which afforded **3a** in only 73% yield (entry 2). The high catalytic activity of the PAFR II catalysts under microwave irradiation was attributed to the presence of polar functional groups, which more efficiently absorb microwaves. The catalyst remained effective even at a sulfur loading of 100 mol ppm, producing **3a** in 79% yield (entry 3). This result indicates that the PAFR II catalyst is highly effective for POM depolymerization. An evaluation of several acid catalysts for POM degradation demonstrated the superior catalytic performance of PAFR II (entries 4–10). The polymeric acid catalyst poly(4-styrenesulfonic acid) (PSS, Fig. 2) afforded **3a** in 71% yield (entry 4). The use of *p*-toluenesulfonic acid (PTSA), *p*-chlorosulfonic acid (PCSA) and phenol as catalysts afforded **3a** in low yields of 19%, 40%, and 4%, respectively (entries
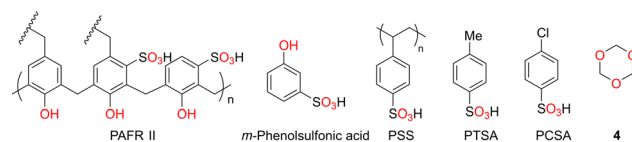

Fig. 2 Structure of the acid catalysts and the reaction intermediate in Table 1.

5–7). Interestingly, the monomeric *m*-phenolsulfonic acid was less effective than the polymeric PAFR II catalyst, affording **3a** in 34% yield (entry 8). Formic acid and sulfuric acid catalysts afforded **3a** in 75% and 64% yields, respectively (entries 9 and 10), and the reaction intermediate 1,3-trioxane (**4**) (Fig. 2) was detected in 31% and 9% yields, respectively (entries 9 (31%) and 10); moreover, polymer **1** was consumed. In all other reactions using homogeneous acid catalysts, unreacted polymer **1** remained. No reaction was observed in the absence of a catalyst (entry 11).

Reactivity of diols and diamines

Under the optimal reaction conditions, the reactivity of **1** with various biomass-derived diols and diamines was explored (Fig. 3). The reaction of **1** with 1,3-propanediol (**2a**) afforded 1,3-dioxane (**3a**) in 99% yield. The degradation of **1** was performed using butane-1,3-diol (**2b**), pentane-2,4-diol (**2c**), ethane-1,2-diol (**2d**), propane-1,2-diol (**2e**), and pinacol (**2f**) to afford the corresponding 1,3-dioxacyclic compounds **3b–g**. The observed trend indicates that primary alcohols demonstrate higher reactivity than sterically hindered secondary and tertiary alcohols. The formation of thermodynamically stable six-membered rings resulted in more efficient POM upcycling than the formation of five- or seven-membered rings. Interestingly, the diamines also produced aminals under this polymeric acid-catalyzed POM upcycling. When reaction was performed using 2,2-dimethyl-1,3-propanediamine (**2h**), the corresponding **3h** was observed in 99% yield.

Reactivity of alcohols and water

Common and environmentally sustainable alcohols such as ethanol and methanol facilitated the depolymerization of **1** (Fig. 4). The reaction of **1** with ethanol required a slightly higher catalyst loading (0.1 mol% S), but afforded diethoxymethane (**5**)

Table 1 Synthesis of 1,3-dioxane from polyoxymethylene (**1**)

Entry	Deviations from standard conditions	Yield of **3a** (%)
1	None	99
2[a]	130 °C conventional heating	73
3	100 mol ppm of PAFR II	79
4	PSS catalyst	71
5	PTSA catalyst	19
6	PCSA catalyst	40
7	Phenol catalyst	4
8	*m*-Phenolsulfonic acid catalyst	34
9	Formic acid catalyst	75
10[b]	H$_2$SO$_4$ catalyst	64
11	No catalyst	0

Reaction conditions: **1** (400 mg, 13.3 mmol (based on monomer), 1 mol equiv.), **2a** (1.2 mol equiv., 16 mmol), PAFR II (260 mol ppm S), 130 °C (microwave heating), 2 h under aerobic conditions. [a] Reaction time: 6 h. [b] Reaction scale: 28 mmol.
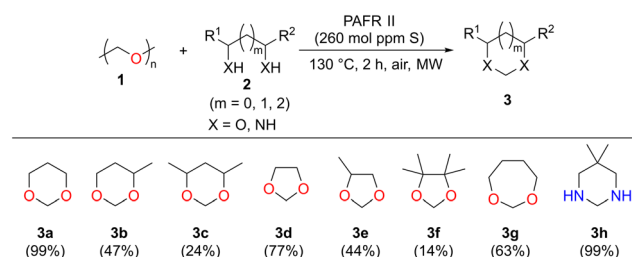

Fig. 3 POM depolymerization of **1** with various diols and diamines (**3a–h**).
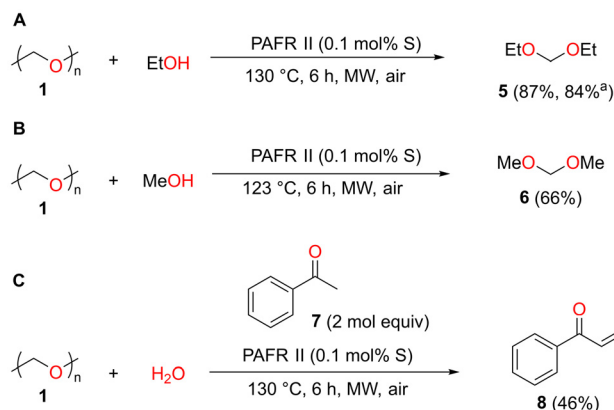
Fig. 4 Reaction of **1** with ethanol, methanol, and water. [a] Polymer **1** originates from a joint clip made from POM. (A) Depolymerization of POM using ethanol. (B) Depolymerization of POM using methanol. (C) Depolymerization of POM using water.

in a relatively high 87% yield (Fig. 4A). Moreover, reacting a POM-based joint clip with ethanol under optimal reaction conditions gave **5** in 84% yield. The reaction of **1** with methanol in the presence of PAFR II at 123 °C, which reached the pressure limit of 10 bar, afforded dimethoxymethane (**6**) in 66% yield (Fig. 4B). The use of water as a nucleophile resulted in complete conversion; however, the desired product was not detected, likely owing to its volatility. To address this issue, formaldehyde was trapped using acetophenone (**7**) *via* a PAFR II-catalyzed aldol condensation, affording **8** in 46% yield (Fig. 4C).

Reactivity of different waste plastics

The formation of **3a** was achieved by upcycling various POM plastic products over 6 h (Fig. 5). A laboratory joint clip readily reacted with **2a** in the presence of PAFR II, affording **3a** in 88% yield (entry 1). The reaction of plastic buckles obtained from a backpack and a polyacetal gear gave **3a** in yields of 67% and 82%, respectively (entries 2 and 3). Similarly, the depolymerization of a black joint and white tube made from POM afforded **3a** in 95% and 56% yields, respectively (entries 4 and 5).

Depolymerization of CFRPs and microplastics

Depolymerizing the POM moiety of carbon-fiber-reinforced polymers (CFRPs), which are known for their strength, water repellency, and corrosion resistance, is crucial for recovering high-value carbon fibers *via* POM upcycling. The POM moiety is depolymerized by PAFR II acid catalysis (Fig. 6A). The reaction of CFRP (10% carbon-fiber-reinforced polymer) with **2a** under the standard reaction conditions afforded **3a** in 71% yield, and reinforced carbon fiber was recovered in 83% yield. The solid-state ^{13}C-NMR spectra indicated that the recovered carbon fibers contained no POM (SI). The Scanning Electron Microscopy (SEM) analysis of the recovered carbon fiber showed needle-like materials. Microplastics are potentially hazardous to human health and pose a significant risk of environmental pollution. To address this, we investigated the
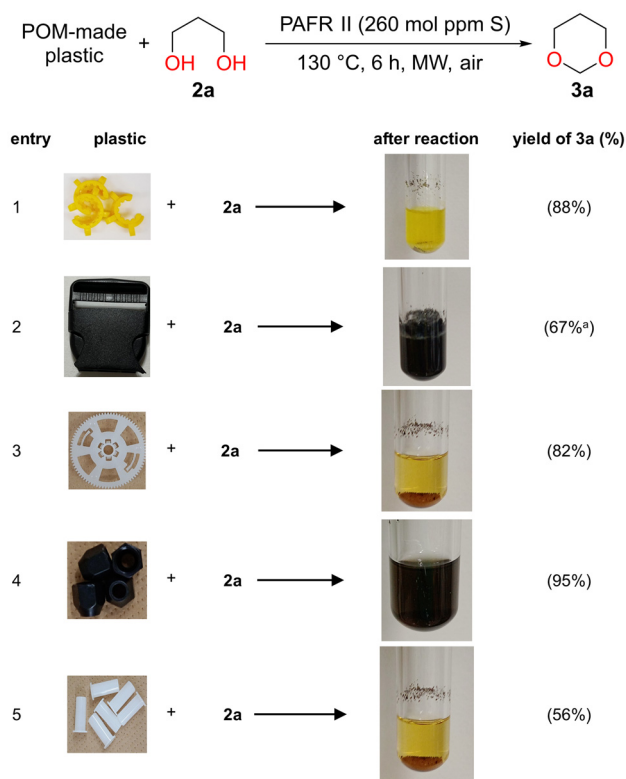

Fig. 5 Upcycling of plastic materials made from POM. Reaction conditions: plastics (400 mg, 13.3 mmol, considered as pure POM material), **2a** (1.2 mol equiv.), PAFR II (260 mol ppm S) under microwave irradiation (80 W) at 130 °C for 6 h. All yields are NMR yields using 1,3,5-trimethoxybeneze as an internal standard. [a] Catalyst loading: 1 mol%.
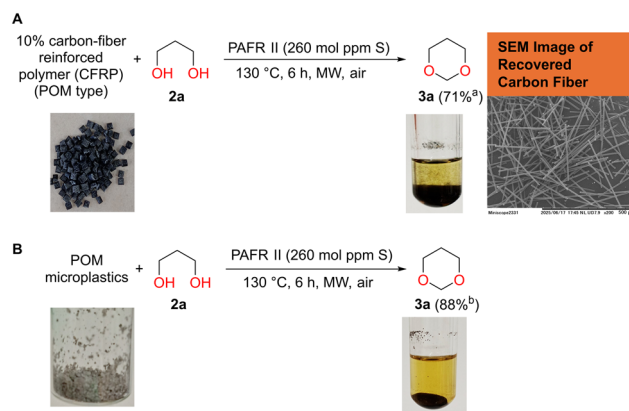

Fig. 6 Upcycling of 10% CFRP and POM microplastics. Reaction conditions: plastics (400 mg, 13.3 mmol, considered as pure POM material), **2a** (1.2 mol equiv.), PAFR II (260 mol ppm S) under microwave irradiation (80 W) at 130 °C for 6 h. All yields are NMR yields using 1,3,5-trimethoxybeneze as an internal standard. [a] 10% carbon fiber was considered the only additive. [b] Microplastic was prepared by ball-milling of black polyacetal joints. (A) Upcycling of carbon-fiber-reinforced polymer (CFRP). (B) Upcycling of POM microplastics.

acid-catalyzed decomposition of microplastics (Fig. 6B). The reaction of microplastics prepared from black polyacetal joints *via* ball milling and with **2a** under the optimized catalytic con-

ditions afforded **3a** in 88% yield. These results demonstrate the efficacy of this approach in facilitating the degradation of microplastics, offering a potential solution to this pressing environmental challenge.

Scale-up upcycling of waste plastics

The upcycling of polyoxymethylene was effective on a 5-gram scale without an increase in catalyst loading. The conversion of waste polyacetal joints (5 g) afforded **3a** in 89% yield (Fig. 7A). Similarly, the upcycling of 10% carbon-fiber-reinforced POM (5 g) containing 500 mg of carbon fibers gave **3a** in 68% yield (Fig. 7B). The carbon fibers were recovered from the reaction mixture in 96% yield, demonstrating the efficiency of this approach for both polymer depolymerization and carbon fiber recovery. Interestingly, our method also successfully upcycled waste polyacetal joints on a 40-gram scale, yielding 89% of **3a** (Fig. 7C). Even this 40-gram scale reaction does not demand increased catalyst loading or higher reaction temperature.

Reusability of PAFR II catalyst

The reusability of the PAFR II catalyst was also investigated (Fig. 8). The catalyst was recovered by filtration; it was washed and dried under vacuum prior to reuse (SI). The catalyst was used six times without any loss of activity, affording **3a** in 97–99% yields. Elemental analysis confirmed the exceptional stability of the PAFR II catalyst under optimal reaction conditions. After six cycles, the recovered catalyst retained a sulfur content of 10.4%, similar to the 11.2% sulfur content of the fresh catalyst, indicating minimal loss of active components. SEM analysis revealed no morphological differences between the fresh and the recovered catalysts (Fig. S10). Likewise, FT-IR spectra indicated that the structural features of the PAFR II catalyst remained unchanged after reuse (Fig. S11). PAFR II
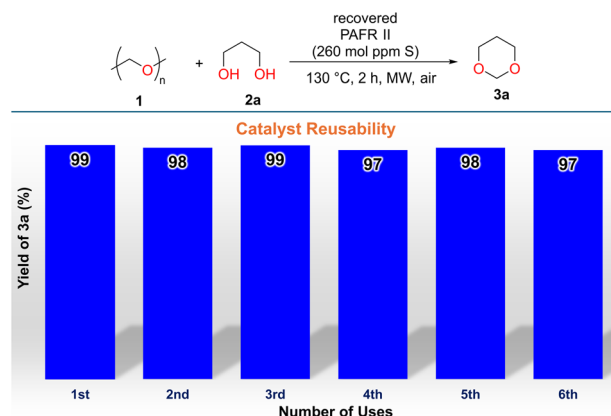

Fig. 8 Reusability of PAFR II in the reaction of **1** with **2a**.

retained its catalytic activity during the upcycling of POM-based joint clips (Table S2), confirming its high reusability. Notably, after three cycles, the reused catalyst PAFR-II afforded **3a** in 88% yield, which was identical to the yield obtained using the fresh catalyst. These results highlight the remarkable durability and sustained catalytic activity of PAFR II in the upcycling of plastic waste, thereby demonstrating its potential for sustainable chemical recycling.

The synthetic utility of the upcycled products obtained using PAFR II was also explored (Fig. 9). The reaction of ethylal (formaldehyde diethyl acetal) (**5**) with 1,4-dimethoxybenzene (**9**) in the presence of PAFR II (1 mol% S), afforded DMpillar[5] arene **10**, an important molecule in host–guest chemistry,[40] in 63% yield (Fig. 9A, top). The insecticide chlorfenapyr (**12**)[41] was obtained in 55% yield via the reaction of **5** and **11** (Fig. 9A, bottom). In addition, we also synthesize compound **14** in one-pot with 81% yield, which is a herbicide (Fig. 9B).[42] Thus, the
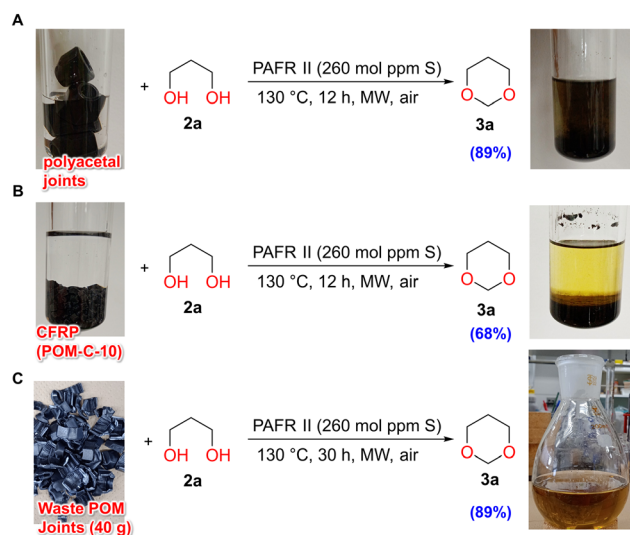

Fig. 7 Scale-up for POM and CFRP upcycling. (A) 5 g-scale depolymerization of polyacetal joints. (B) 5 g-scale upcycling of POM-C-10 (10% carbon-fiber-reinforced polymer, CFRP), (C) 40 g-scale upcycling of waste polyacetal joints.
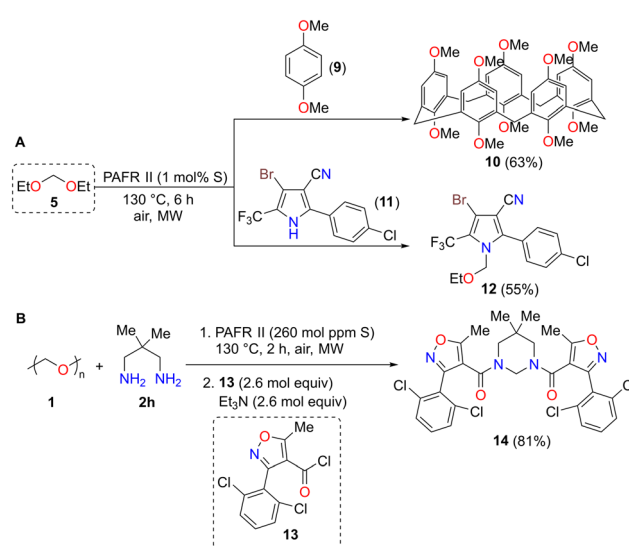

Fig. 9 Synthesis of value-added chemicals. (A) Stepwise synthesis of DMpillar[5]arene (top) and stepwise synthesis of chlorfenapyr (bottom). (B) One-pot synthesis of herbicide (**14**).
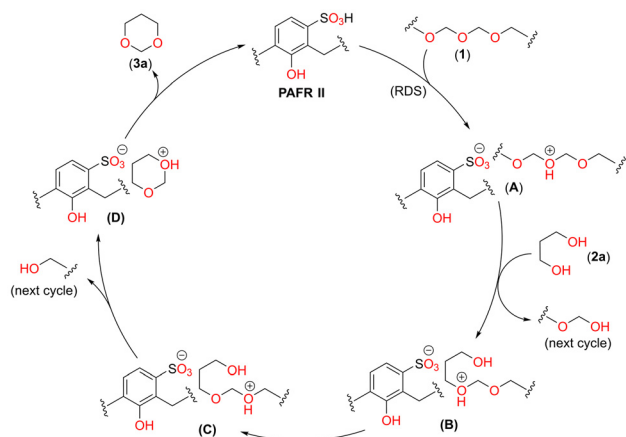
Fig. 10 Plausible catalytic pathway for POM upcycling.

PAFR II-catalyzed POM upcycling strategy converted waste plastic materials into value-added chemicals.

Plausible catalytic pathway

The chemical kinetic studies suggest that the POM upcycling process follows a first-order dependence for the polymer (**1**) (Fig. S15) and the catalyst (Fig. S13), whereas it follows a zero-order dependence for 1,3-propanediol (**2a**) (Fig. S14). Thus, based on chemical kinetics, the interaction between two solid materials (PAFR II catalysts and polymer) is the rate-determining step for this conversion. A plausible catalytic pathway (Fig. 10) is proposed based on mechanistic studies (SI, Section S11) and chemical kinetics. Initially, PAFR II interacts with polyoxymethylene (**1**) to form an oxonium ion intermediate **B**. Formation of this oxonium ion intermediate is also observed by IR (Fig. S16). Next, 1,3-propanediol (**2a**) acts as a nucleophile and forms intermediate **B**. A proton exchange generates intermediate **C** from intermediate **B**. Next, intermediate **D** is generated *via* an intermolecular cyclization, followed by another proton exchange to regenerate the catalyst and produce 1,3-dioxane (**3a**) as a product.

Life cycle assessment analysis

The life cycle assessment (LCA) analysis reveals that our POM upcycling strategy results in significantly lower greenhouse gas emissions (1.88 kg CO_2-eq per kg) compared to traditional methods of 1,3-dioxane synthesis (6.08 kg CO_2-eq per kg), indicating that our method is more environmentally friendly and sustainable (see SI, Section 12). Moreover, the incineration of polyoxymethylene can be avoided by directly converting the plastics to value-added chemicals, which also makes the upcycle strategy sustainable.

Conclusions

In this study, we successfully achieved the upcycling of waste polyoxymethylene (POM) plastics using a novel polymeric heterogeneous catalyst. This approach enabled the efficient depolymerization of POM in the presence of diols, ethanol, methanol, or water, with a remarkably low catalyst loading of 260 mol ppm. The PAFR II catalyst exhibited outstanding stability and maintained essentially 100% catalytic activity for at least six cycles. This method is a powerful and scalable strategy for the upcycling of waste polyacetal plastics into value-added chemicals and demonstrates versatility across both small- and large-scale applications. Moreover, the catalytic system exhibits broad utility, enabling the synthesis of high-value pillar[5] arenes, insecticides, and herbicides. Building on this success, ongoing research in our laboratory continues to expand the frontier of plastic upcycling and explore the potential of PAFR II catalysts in a wide range of sustainable polymer transformations. Additionally, we plan to design a new sulfur-bearing catalyst for more efficient plastic upcycling.

Author contributions

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information (experimental procedures, product characterization, catalyst reusability, life cycle assessments, ^{1}H-NMR, ^{13}C-NMR, ^{13}C-CPMAS, IR spectra, GC and GC-MS, MALDI-MS spectra) is available. See DOI: https://doi.org/10.1039/d5gc06065f.

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