

CHEMISTRY

Molecular catalyst systems as key enablers for tailored polyesters and polycarbonate recycling concepts

Stefan Westhues, Jasmine Idel, Jürgen Klankermayer*

A transition metal catalyst system for the selective catalytic depolymerization of various polyester- and polycarbonate-based materials is presented. The use of a molecular ruthenium catalyst with selected triphos ligands enabled a selective hydrogenolysis of a large diversity of polymeric consumer products, paving the way to innovative and sustainable recycling strategies within a circular economy.

INTRODUCTION

A wide range of synthetic polymers are currently produced and designed to meet the various needs and requirements of industry and consumers. The raw materials for these durable products are predominantly centered on petroleum resources, and only recently is the possibility to use bio-based alternatives being industrially explored (1). Moreover, the steadily increasing production and use of these polymers are largely unsustainable, as efficient recycling strategies for these nonbiodegradable materials remain elusive (2). This results in a tremendous growth of waste plastics, and the environmental pollution with the respective material is becoming an enormous problem. Consequently, current research is trying to develop new strategies to either substitute traditional polymers by bio-based alternatives or effectively recycle postconsumer plastics. However, the former approach would not lead directly to sustainable polymers and a waste-free economy, as these new polymeric materials are often accompanied by comparable end-of-life problems. The direct reuse of polymeric matter is the straightforward approach, but rather limited to only selected applications. Regarding thermoplastic polymers, mechanical recycling can be accomplished by melting and remolding, representing a useful strategy for certain applications. However, despite the losses in polymer quality, political regulations on food packaging prevent a closed-loop recycling, exemplified on the difficult reuse of polyethylene terephthalate (PET) (3). Thus, almost 70% of post-consumed PET is currently used for the production of synthetic fibers (4). A more promising approach is the chemical recycling through depolymerization, but current chemical strategies such as hydrolysis (5–7), methanolysis (8, 9), and glycolysis (5, 10, 11) are not cost-competitive with the use of new petrol-based monomers (12).

Consequently, the European Environmental Agency is fostering research toward a “circular economy” with effective recycling strategies as a core task (13). The recycling strategies envisage a selective process in which polymer wastes are depolymerized back to their starting monomer. These compounds are then purified and reused to yield polymeric materials with comparable quality or to define educts/building blocks for new value-added polymeric products (14, 15).

The groups of D. Milstein and J. Robertson initiated research in this direction and used homogeneous catalysts with molecular hydrogen for a catalytic depolymerization of polyesters to alcohol monomers (16, 17). They presented a successful attempt of catalytic polymer breakdown via hydrogenolysis, using ruthenium-N,N,P-pincer complexes in the presence of base, and obtained high yields of the respective mono-

meric products. Later, T. Cantat extended this approach and used hydrosilanes as reduction equivalents to hydrogenate selected polymers (18). More recently, the group of M. Clarke enhanced the hydrogenolysis of PET by using innovative ruthenium-N,N,P-pincer complexes. However, high catalyst loadings, complex solvents, and long reaction times hamper so far the translation of this approach to consumer products and engineered polymers (19).

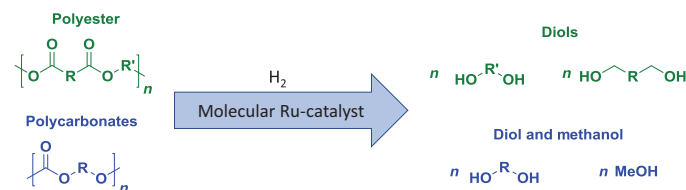
Herein, the selective catalytic hydrogenolysis using a molecular ruthenium complex of a variety of the most abundant polyester and polycarbonate polymers is presented, resulting in novel possibilities for efficient polymer recycling within a circular economy approach (Scheme 1).

Recently, effective molecular catalysts for the reduction of challenging functionalities could be developed, exemplified by the highly versatile and stable ruthenium complex [Ru(triphos)tmm] [A, triphos = (1,1,1-tri(diphenylphosphinomethyl)ethane, tmm = trimethylenemethane) as privileged system. This important advancement moved this molecular catalyst, and especially recently optimized catalyst structure [Ru(triphos-*xy*)tmm] [B, triphos-*xy* = 1,1,1-tri(bis(3,5-dimethylphenyl)phosphinomethyl)ethane], into the spotlight for novel transformations and in special cases closer to the harsher processing conditions of heterogeneous catalyst systems (20, 21). Consequently, the application of these systems in the challenging transformation of robust and stable polymeric materials was envisaged, using molecular hydrogen for the respective hydrogenolysis reaction.

RESULTS AND DISCUSSION

In a first set of experiments, the selected polyester and polycarbonate materials were used for the initial investigations (for details on polymer grade, see the Supplementary Materials). Referring to the repetition unit of the polymers, 1 mmol of each polymer granulate was transformed, using 1 mole percent (mol %) catalyst and bis(trifluoromethanesulfonyl)imide (HNTf₂) as cocatalyst in 1,4-dioxane (Table 1).

The first reaction was conducted in the presence of catalyst A with the aliphatic polyester polylactic acid (PLA, 1). In this transformation,



Scheme 1. Reductive depolymerization of polymeric waste with a molecular ruthenium catalyst.

Institut für Technische und Makromolekulare Chemie, Rheinisch-Westfälische Technische Hochschule Aachen, Aachen University, Worringerweg 2, 52074 Aachen, Germany.

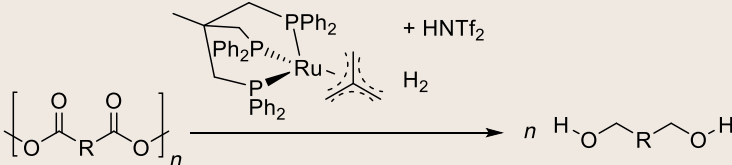
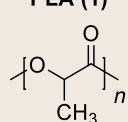
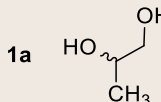
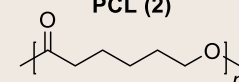
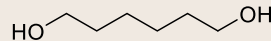
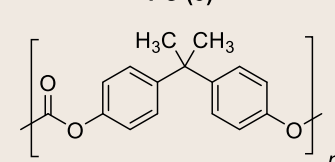
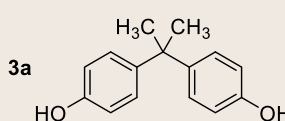
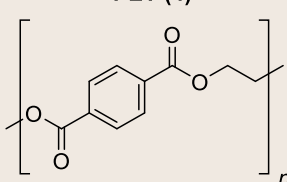
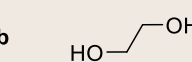
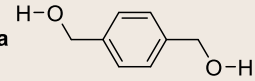
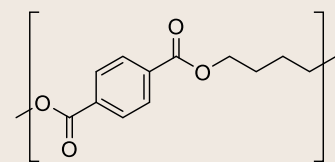
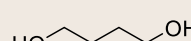
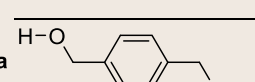
*Corresponding author. Email: jklankermayer@itmc.rwth-aachen.de

Copyright © 2018
The Authors, some
rights reserved;
exclusive licensee
American Association
for the Advancement
of Science. No claim to
original U.S. Government
Works. Distributed
under a Creative
Commons Attribution
NonCommercial
License 4.0 (CC BY-NC).

full conversion could be achieved, and only 1,2-propanediol (**1a**) was obtained as product, confirming the suitability of this molecular catalyst for the hydrogenolysis of polyesters (Table 1, entry 1). Subsequently, polycaprolactone (PCL, **2**) was converted in a high-pressure autoclave, and only 1,6-hexanediol (**2a**) could be detected in the product mixture (Table 1, entry 2). Exemplarily for polycarbonates, the most abundant representative, based on bisphenol A (PC, **3**), was hydrogenated using [Ru(triphos)tmm] and HNTf₂ as catalyst system. The application of former stated reaction conditions gave full conversion toward bisphenol A (**3a**) and methanol (**3b**; Table 1, entry 3). The hydrogenolysis of PET (**4**), the most common polyester, was more challenging,

and only 42% conversion with a good selectivity of 64% toward 1,4-benzene dimethanol (**4a**) and ethylene glycol (**4b**) was achieved (Table 1, entry 4). Besides the formation of the respective diols, the acid-activated catalyst tends to catalyze the consecutive formation of ether products, strongly reducing the selectivity of the transformation. This effect was even more pronounced in the hydrogenolysis of polybutylene terephthalate (PBT, **5**), where the polymeric material was fully converted, but only 22% of product could be assigned to the monomeric diols **4a** and 1,4-butanediol (**5b**; Table 1, entry 6) (22). In these reactions, nuclear magnetic resonance (NMR) studies of the postreaction solution revealed the formation of a catalyst dimer and

Table 1. Hydrogenolysis of selected polyesters and polycarbonate material using [Ru(triphos)tmm] (A) or [Ru(triphos-xyt)tmm] (B) and HNTf₂.*

				
Entry	Conversion (%)†	Selectivity (%)†	Polymer	Product
PLA (1)				
1	>99	>99		1a 
PCL (2)				
2	>99	>99		2a 
PC (3)				
3	>99	>99		3a  3b MeOH
PET (4)				
4	42	64		4b 
5†	64	>99		4a 
PBT (5)				
6	>99	22		5b 
7†	>99	>99		4a 

*Reaction conditions: H₂ (100 bar), polymer (1 mmol; calculated on the repetition unit), 1 mol % [Ru(triphos)tmm] (A) and HNTf₂, 3 ml of 1,4-dioxane, 140°C, 16-hour reaction time. †Conversion and selectivity were determined by ¹H NMR spectroscopy using mesitylene as internal standard. ‡[Ru(triphos-xyt)tmm] (B) (1 mol %) was used instead of A.

connected liberation of free acid as basis for the strongly enhanced etherification.

Consequently, a molecular catalyst suppressing these side reactions, should be established, enabling the selective formation of monomeric alcohols in the product solution. Recently, we introduced a ruthenium triphos complex showing higher activity and stability in many challenging hydrogenation reactions (20). The use of this modified catalyst **B** in the hydrogenolysis of PET (Table 1, entry 5) and PBT (Table 1, entry 7) confirmed the assumptions and excellent selectivity toward the respective diol species could be obtained in both cases.

In the subsequent development step, selected consumer products based on these polymers were investigated. As depicted in Fig. 1, various transparent or nontransparent (indicating partly crystalline domains in the respective material) PET sources were used. Thus, in the first set of experiments, a commercially available water bottle was cut into pieces and either shredded in a freeze mill or directly used without any further pretreatment. Subjecting those PET flakes (4) to the established reaction conditions gave full conversion with excellent selectivity (>99%) toward the diols **4a** and **4b** (Table 2, entry 1). Subsequently, the catalyst loading was decreased to 0.2 mol %, and again full conversion of the challenging substrate **4** could be obtained (Table 2, entry 2). Since remarkable results could be obtained with PET derived from a standard water bottle, PET based on other customary sources was tested.

In detail, PET from a dyed soda bottle (Table 2, entry 3), a synthetic pillow filling (Table 2, entry 4), and a yoghurt pot (Table 2, entry 5) were used as complex starting materials. Before the hydrogenolysis reaction, the polymers were cut into pieces and used without any further treatment, as depicted in Fig. 1. As the substrates were only poorly soluble in the indicated solvents, the reaction had to be performed with the swollen polymers. Gratifyingly, all tested consumer products were fully converted to the diols **4a** and **4b** with excellent selectivity. In a challenging experiment, the depolymerization conditions were applied to a sport jersey, and again full conversion with a selectivity of 86% was

obtained (Table 2, entry 6). These results indicate the broad applicability of the approach and, additionally, the negligible influence of polymer additives and color pigments on the catalyst activity.

After the successful demonstration of catalytic hydrogenolysis of polymers with catalyst structure **B**, the optimization of the system with respect to catalytic activity was targeted, paving the way to a broader applicability. In the first approach, PBT could be completely hydrogenated with a low catalyst loading of 0.2 mol % [Ru(triphos-*xy*)tmm] **B**/HNTf₂ (Table 3, entry 1). Second, PLA granulate was fully hydrogenolyzed using an even lower catalyst loading of 0.01 mol %, giving a maximum turnover number (TON) of 10,000 (Table 3, entry 2). Striving toward the depolymerization of consumer products, PLA obtained from a beverage cup, was used for further experiments. However, repeating the former experiment with customary PLA gave only 35% conversion (Table 3, entry 3) (for further information, see the Supplementary Materials). Thus, the reaction medium was altered, and excellent performance was observed with 1,2-propanediol as a solvent, yielding full conversion under standard hydrogenolysis conditions with 0.1 mol % [Ru(triphos)tmm] **A**/HNTf₂ (Table 3, entry 4), facilitating the subsequent purification and downstream processing.

The second pure aliphatic polyester, PCL, could be hydrogenated to **2a** with a low catalyst loading of only 0.02 mol % (Table 3, entry 5). Because of its rather low melting point (*T_m*, ~65°C) and high decomposition temperature (*T_D*, ~350°C), the hydrogenolysis was performed at 140°C in the polymer melt and thus in the absence of external solvent (23). This resulted in 64% conversion (TON 3167) toward **2a** (Table 3, entry 6; for further experiments, see the Supplementary Materials). Demonstrating the application of the polycarbonate hydrogenolysis on consumer products, a compact disc (CD) and a regular beverage cup were subjected to the hydrogenolysis conditions. Although commercially available PC contains impurities such as labeling dye, aluminum coating, or metallic glitter, it could be fully converted to **3a** and **3b** using only 0.33 mol % [Ru(triphos)tmm]/HNTf₂ (Table 3, entries 7 and 8).

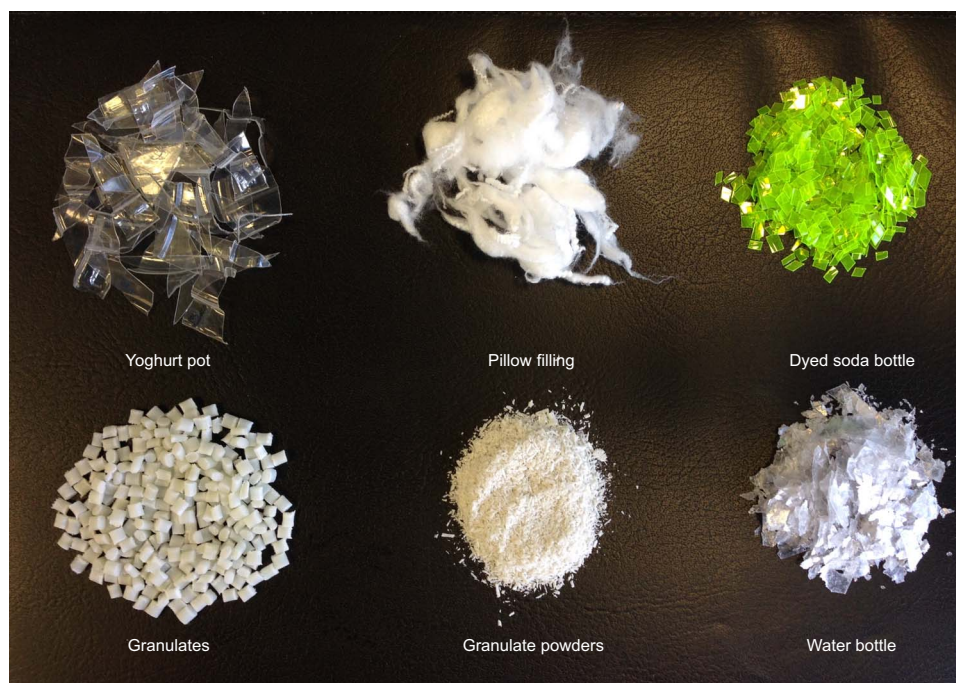
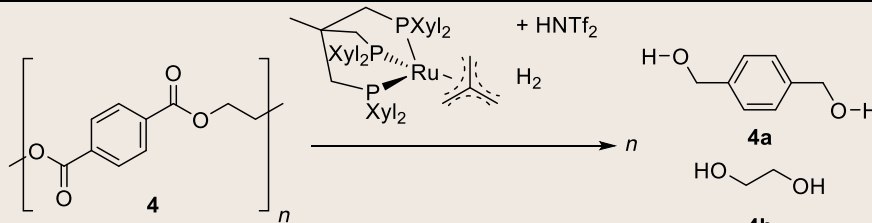


Fig. 1. Overview of the commercially available PET sources used for the catalytic hydrogenolysis.

Table 2. Hydrogenolysis of PET of commercially available sources using [Ru(triphos-xyl)tmm] (B)/HNTf₂ as catalyst.*


The reaction scheme shows the hydrogenolysis of PET (4) using catalyst B, [Ru(triphos-xyl)tmm], and HNTf₂ under H₂ to produce 4a and 4b. The catalyst structure is shown as a ruthenium center coordinated by a tris(phosphine) ligand with xyl groups and a tmm ligand. The reaction yields n molecules of 4a and 4b.

Entry	Conversion (%)†	Selectivity (%)†	Polymer source	Catalyst B (mol %)
1	>99	>99	Water bottle	1
2	>99	>99	Water bottle	0.2
3	>99	98	Dyed bottle	0.5
4	>99	99	Pillow filling	0.5
5	>99	>99	Yoghurt pot	0.5
6	>99	86	Sport jersey	0.5

*Reaction conditions: H₂ (100 bar), PET (2 mmol), 1 equivalent HNTf₂ related on the catalyst [Ru(triphos-xyl)tmm] (B), 16 hours, 140°C, 4 ml of 1,4-dioxane. †Conversion and selectivity were determined by ¹H NMR spectroscopy using mesitylene as internal standard.

Table 3. Hydrogenolysis of polymer granules and commercially available products using [Ru(triphos)tmm] (A)/[Ru(triphos-xyl)tmm] (B) and HNTf₂ as catalyst.*

Ar = Ph, Xyl
+ HNTf₂

H₂

n H-O-CH₂-CH₂-R-O-H

Entry	Yield (%)†	Polymer type	Substrate (mmol)	Catalyst (mol %)	Solvent (ml)	
1	4a	>99	PBT granulate	5	B 0.2	4
2	1a	>99	PLA granulate	10	A 0.01	4
3	1a	35	PLA beverage cup	10	A 0.01	4
4‡	1a	>99	PLA beverage cup	10	A 0.1	3
5	2a	>99	PCL granulate	25	A 0.02	5
6	2a	64	PCL granulate	25	A 0.02	—
7	3a	>99	PC CD	2	A 0.33	6
8	3a	>99	PC beverage cup	2	A 0.33	6

*Reaction conditions: H₂ (100 bar), x mol % [Ru(triphos)tmm] (A)/[Ru(triphos-xyl)tmm] (B) and HNTf₂, 16-hour reaction time, 140°C, x ml of 1,4-dioxane. †Yield was determined via ¹H NMR spectroscopy using mesitylene as internal standard.

‡Reaction was performed in 3 ml of 1,2-propanediol.

The properties of plastics are often tailored to the respective application by blending different polymers in the production procedure, either via a mechanical or a chemical process. This complexity in the material transforms the selective upcycling of those waste plastics into an even greater challenge. Thus, in the course of our investigations, the impact of complex polymer mixtures on the catalytic depolymerization reaction was tested. In the presence of polypropylene (PP), polyethylene (PE), nylon (PA 6), polyvinylchloride (PVC), or polystyrene (PS), the hydrogenolysis of PET was repeated under standard conditions. In

these challenging experiments, full conversion of PET to 4a/4b was observed, and none of the described additional polymers hampered the selective depolymerization of the polyester. Moreover, most of the tested additional nonpolyester polymers were insoluble in 1,4-dioxane, opening a convenient pathway toward polymer separation.

On the basis of these findings, in the next development step, the separation of different polyesters via hydrogenolysis was investigated. 2 mmol PET and PLA from customary sources were depolymerized at different reaction temperatures (Fig. 2, top). Reaction temperatures of

140° and 120°C led to the full hydrogenolysis of both polymers, but lowering the reaction temperature resulted in a decreased conversion of PET, maintaining full conversion of PLA. Then, at 45°C, PET remained unconverted, while PLA got fully depolymerized (Fig. 2, top). Gratifyingly, this selectivity could also be achieved at 140°C if the solvent was changed to 1,2-propanediol **1a**. Because of its insolubility in 1,2-propanediol and 1,4-dioxane, PET can be easily filtered off the

reaction solution and depolymerized in a subsequent reaction. Consequently, this approach enables catalytic hydrogenolysis as a method to transform complex polymer mixtures by taking into consideration the respective physicochemical properties of the starting materials (Fig. 2, bottom).

In the final experiments, the possibility to translate this development to a larger scale was investigated. Thus, a complete coated PLA beverage

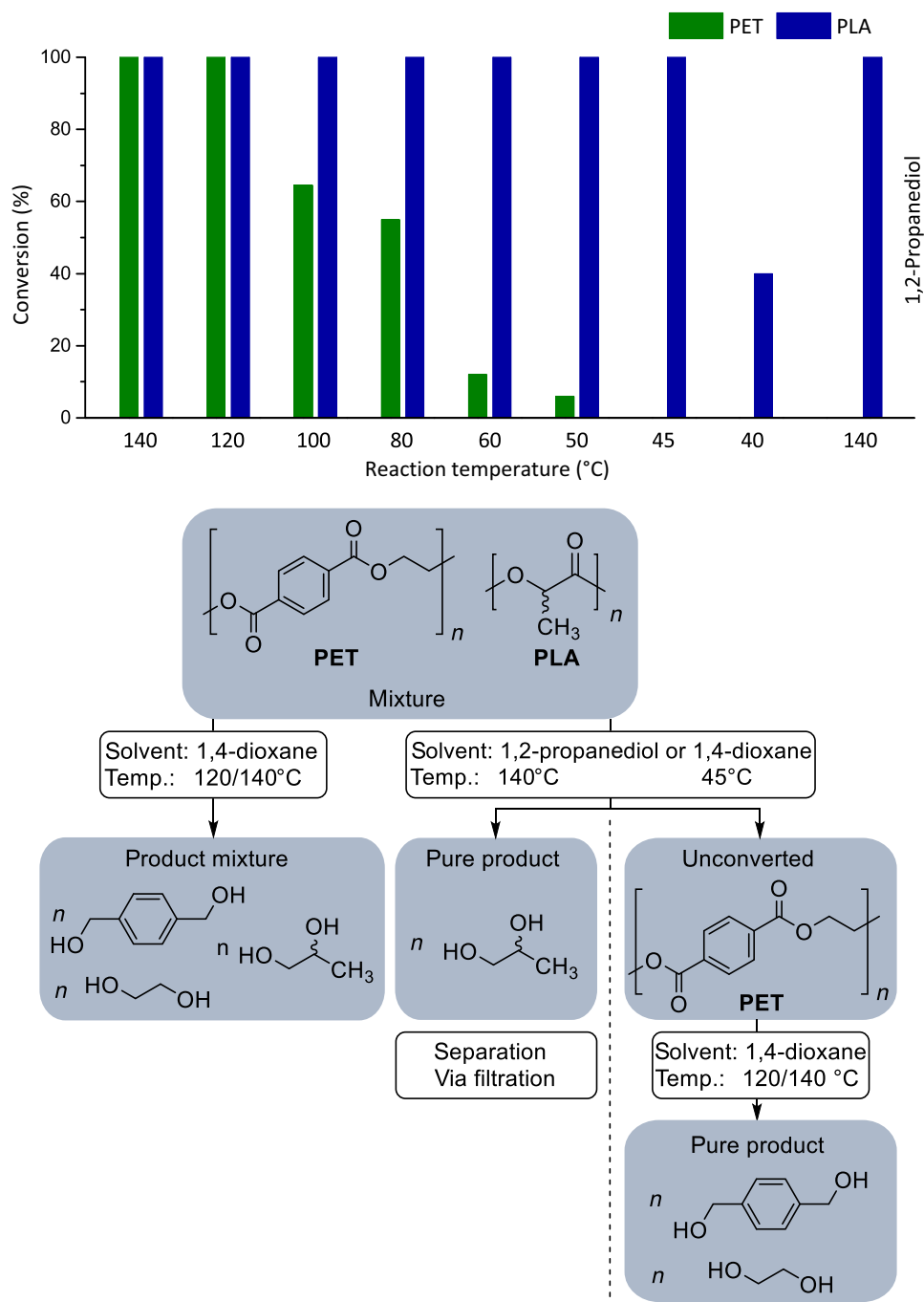


Fig. 2. Selective separation of two different polyesters via the catalytic hydrogenolysis approach. Top: Selective polymer hydrogenolysis of PLA and PET using [Ru(tri(phenyl)silyl)methylallyl]NTf₂; reaction conditions: PLA (2 mmol), PET (2 mmol), [Ru(tri(phenyl)silyl)methylallyl]NTf₂ (10 μmol), 1,4-dioxane (4 ml), H₂ (100 bar), 16 hours. Conversion and selectivity were determined by ¹H NMR spectroscopy using mesitylene as internal standard. Bottom: Flow diagram, illustrating the envisioned processing of polymer mixtures.

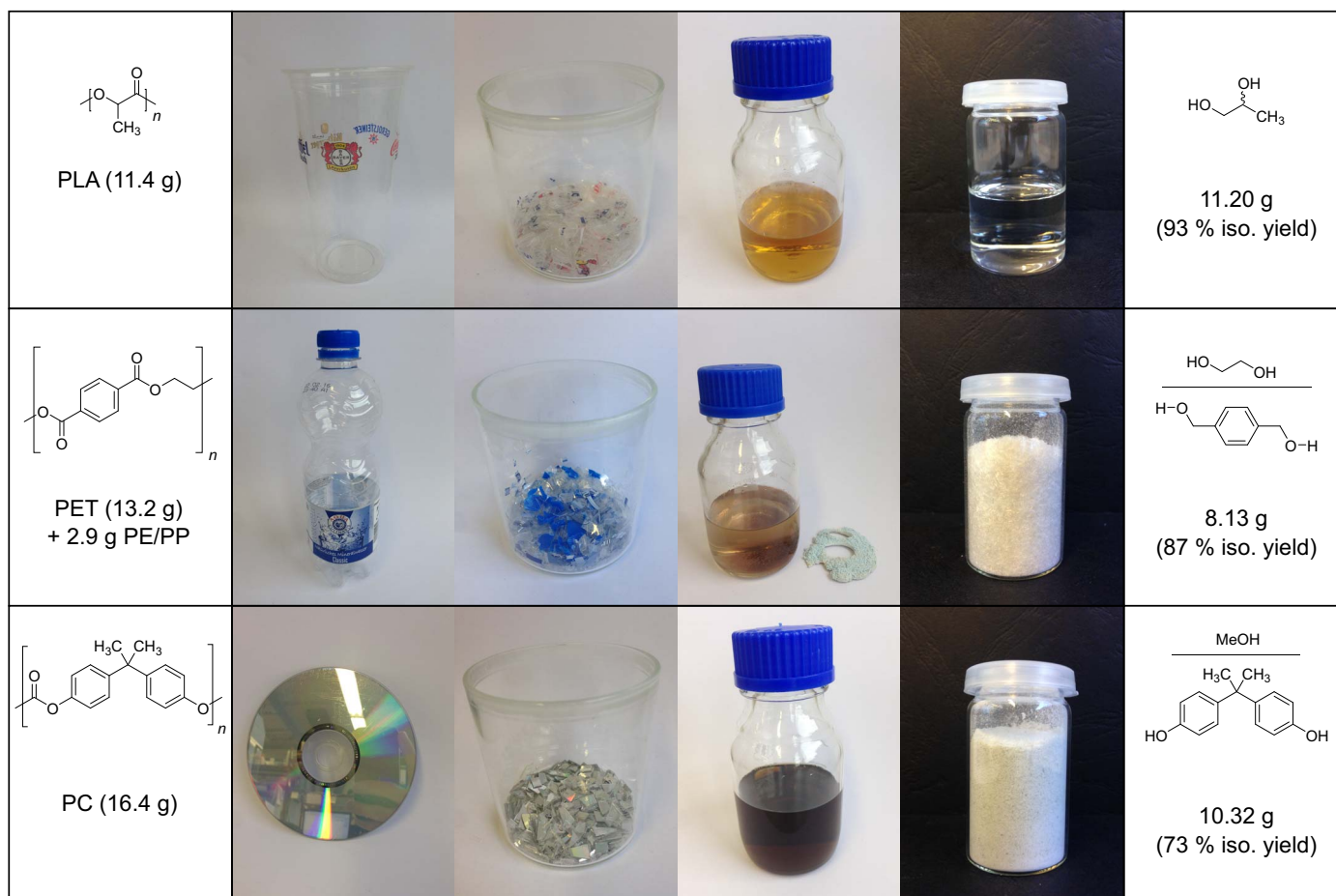


Fig. 3. Hydrogenolysis up-scaling for selected polyesters and polycarbonate consumer products.

Table 4. Hydrogenolysis scale-up of consumer polymer products using [Ru(triphos)tmm] (A)/[Ru(triphos-*xy*)tmm] (B) and HNTf₂*.

Entry	Conversion (%) [†]	Selectivity (%) [†]	Polymer source (g)	Catalyst (mol %)
1	>99	>99	Drinking cup, PLA (11.4)	A 0.05
2 [‡]	>99	98	0.5-Liter water bottle, PET (13.2) + screw cap, PP and labeling, PE (2.9)	B 0.2
3 [‡]	>99	>99	0.5-Liter water bottle, PET (13.2)	B 0.1
4	>99	>99	CD, PC (16.1)	A 0.5

*Reaction conditions: The reactions were performed in a 500-ml steel autoclave using 16-hour reaction time, *x* mol % [Ru(triphos)tmm] (A) and HNTf₂, 140°C, 120 ml of 1,4-dioxane, and 90-bar constant hydrogen pressure. [†]Conversion and selectivity were determined by ¹H NMR spectroscopy using mesitylene as internal standard. [‡][Ru(triphos-*xy*)tmm] (B) and HNTf₂ were used.

cup was cut into pieces and subjected to the established hydrogenolysis conditions in a 500-ml autoclave (Fig. 3 and Table 4). Gratifyingly, at a low catalyst loading of 0.05 mol % [Ru(triphos)tmm] **A**/HNTf₂, full conversion to 1,2-propanediol **1a** could be achieved, highlighting the feasibility of the novel approach (Fig. 3, top row, and Table 4, entry 1). Solids originating from the labeling of the cup could be easily filtered off the postreaction solution, as they are insoluble in the solvent. Subsequently, the most abundant polyester, PET, was hydrogenated on a gram scale using an entire 0.5-liter water bottle with screw cap (PP)

and label (PE). Using a rather low catalyst loading of 0.2 mol %, **4** was selectively depolymerized to diols **4a** and **4b**, while PP and PE remained molten but unconverted (Fig. 3, middle row, and Table 4, entry 2). The unconverted polymers were simply filtered off the solution and could be easily transferred to a subsequent recycling process. Performing the reaction in the absence of screw cap and label with only 0.1 mol % catalyst (TON 1000) resulted in full conversion and a homogeneous solution without any residues (Table 4, entry 3). Remarkably, the scale-up experiment allowed a lowering of the minimum catalyst loading, thus

highlighting the possibility for future optimization strategies. In a final reaction, a whole CD was cut into pieces and could be fully converted to **3a** and **3b** using 0.5 mol % [Ru(triphos)tmm]/HNTf₂ (Fig. 3, bottom row, and Table 4, entry 4). Again, the solid residues from the aluminum layer and the coating remained unconverted and could be easily separated by filtration.

CONCLUSION

In conclusion, the effective and selective catalytic depolymerization of waste polyesters/polycarbonates could be established, and the key enabler for this tailored recycling concept was the development of adapted molecular catalyst systems. On the basis of this approach, the polymers from these waste plastics are transformed to the respective value-added diols, enabling a recycling concept within the circular economy vision. Moreover, the detailed studies on a larger scale revealed tolerance of the catalyst toward various polymer additives and even allowed the consecutive transformation and separation of polymer mixtures. In addition, the effectiveness and impact of this method can be enlarged, envisioning a catalytic process with “green hydrogen” from water electrolysis based on renewable energy. Moreover, the catalytic combination of recycled diols with carbon dioxide allows the sustainable synthesis of linear and cyclic acetals only from waste carbon resources (24, 25), and thus, this strategy may pave the way to innovative open-loop recycling methods.

MATERIALS AND METHODS

General procedure for the hydrogenative depolymerization

Polymer (1 mmol; referring to its repetition unit) was filled in a glass insert, equipped with a stir bar, and subsequently placed in a high-pressure stainless steel autoclave. [Ru(triphos)(tmm)] (7.8 mg, 0.01 mmol) or [Ru(triphos-*xy*)tmm] (9.5 mg, 0.01 mmol), HNTf₂ (2.8 mg, 0.01 mmol), and 1,4-dioxane (3 ml) were added through a cannula under argon. Once the autoclave was sealed and pressurized with hydrogen (100 bar), the reaction mixture was stirred for 16 hours at 140°C. Afterward, the reaction was cooled in an ice bath, and the pressure was carefully released. The crude reaction mixture was analyzed by ¹H NMR spectroscopy, using mesitylene as internal standard.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/4/8/eaat9669/DC1>

Section S1. General procedure

Section S2. Synthesis of the catalysts

Section S3. General procedure for autoclave reactions

Section S4. Additional Information

Section S5. NMR spectroscopy data of the products

Section S6. Crude NMR spectra of the products

Section S7. NMR spectra of the isolated products

Table S1. Hydrogenolysis of PLA derived from S-PLA granulate and a beverage cup using [Ru(triphos-derivative)tmm] complexes and HNTf₂.

Table S2. Hydrogenolysis of PET with [Ru(triphos-*xy*)tmm] and HNTf₂ in the presence of a polymer “additive/impurity.”

Table S3. Hydrogenolysis of PCL in the polymer melt using [Ru(triphos)tmm] and HNTf₂.

Table S4. Separation of PLA and PET via selective hydrogenolysis at low temperatures using [Ru(triphos-*xy*)tmm] and HNTf₂.

Fig. S1. Pressure drop curves of the hydrogenolysis of PCL with different molecular weights using [Ru(triphos)tmm] and HNTf₂ as catalyst.

Fig. S2. Pressure drop curve of the hydrogenolysis of polyesters and polycarbonates.

Fig. S3. ¹H NMR spectrum (600 MHz) [0 to 7.5 parts per million (ppm)] of the crude 1,4-dioxane reaction mixture of the PLA (**1**) hydrogenolysis to 1,2-propanediol (**1a**).

Fig. S4. ¹³C NMR spectrum (150 MHz) (0 to 160 ppm) of the crude 1,4-dioxane reaction mixture of the PLA (**1**) hydrogenolysis to 1,2-propanediol (**1a**).

Fig. S5. ¹H NMR spectrum (600 MHz) (0 to 7.5 ppm) of the crude 1,4-dioxane reaction mixture of the hydrogenolysis of PCL (**2**) to 1,6-hexanediol (**2a**).

Fig. S6. ¹³C NMR spectrum (150 MHz) (0 to 160 ppm) of the crude 1,4-dioxane reaction mixture of the hydrogenolysis of PCL (**2**) to 1,6-hexanediol (**2a**).

Fig. S7. ¹H NMR spectrum (400 MHz) (0 to 7.5 ppm) of the crude 1,4-dioxane reaction mixture of the hydrogenolysis of PET (**4**) obtained from a water bottle to benzene dimethanol (**4a**) and ethylene glycol (**4b**).

Fig. S8. ¹³C NMR spectrum (100 MHz) (0 to 160 ppm) of the crude 1,4-dioxane reaction mixture of the hydrogenolysis of PET (**4**) obtained from a water bottle to benzene dimethanol (**4a**) and ethylene glycol (**4b**).

Fig. S9. ¹H NMR spectrum (400 MHz) (0 to 7.5 ppm) of the crude 1,4-dioxane reaction mixture of the hydrogenolysis of PBT (**5**) to benzene dimethanol (**4a**) and 1,4-butanediol (**5b**).

Fig. S10. ¹³C NMR spectrum (100 MHz) (0 to 160 ppm) of the crude 1,4-dioxane reaction mixture of the hydrogenolysis of PBT (**5**) to benzene dimethanol (**4a**) and 1,4-butanediol (**5b**).

Fig. S11. ¹H NMR spectrum (400 MHz) (0 to 7.5 ppm) of the crude 1,4-dioxane reaction mixture of the hydrogenolysis of polycarbonate (bisphenol A) (**3**), obtained from a CD, to 4,4'-(propane-2,2-diyl)diphenol (bisphenol A, **3a**) and methanol (**3b**).

Fig. S12. ¹³C NMR spectrum (75 MHz) (0 to 160 ppm) of the crude 1,4-dioxane reaction mixture of the hydrogenolysis of polycarbonate (bisphenol A) (**3**), obtained from a CD, to 4,4'-(propane-2,2-diyl)diphenol (bisphenol A, **3a**) and methanol (**3b**).

Fig. S13. ¹H NMR spectrum (400 MHz) (0 to 7.5 ppm) of the isolated 1,2-propanediol (**1a**) obtained from a postconsumed beverage cup in CDCl₃.

Fig. S14. ¹³C NMR spectrum (100 MHz) (10 to 230 ppm) of the isolated 1,2-propanediol (**1a**) obtained from a postconsumed beverage cup in CDCl₃.

Fig. S15. ¹H NMR spectrum (400 MHz) (0 to 12.5 ppm) of the isolated bisphenol A (**3a**) obtained from a postconsumed CD in dimethyl sulfoxide (DMSO)-d₆.

Fig. S16. ¹³C NMR spectrum (100 MHz) (0 to 230 ppm) of the isolated bisphenol A (**3a**) obtained from a postconsumed CD in DMSO-d₆.

Fig. S17. ¹H NMR spectrum (400 MHz) (0 to 8 ppm) of the isolated 1,4-benzene dimethanol (**4a**) obtained from a postconsumed PET bottle in a mixture of CDCl₃ and DMSO-d₆.

Fig. S18. ¹³C NMR spectrum (100 MHz) (0 to 210 ppm) of the isolated 1,4-benzene dimethanol (**4a**) obtained from a postconsumed PET bottle in a mixture of CDCl₃ and DMSO-d₆.

REFERENCES AND NOTES

- M. Hong, E. Y.-X. Chen, Chemically recyclable polymers: A circular economy approach to sustainability. *Green Chem.* **19**, 3692–3706 (2017).
- R. Geyer, J. R. Jambeck, K. L. Law, Production, use, and fate of all plastics ever made. *Sci. Adv.* **3**, e1700782 (2017).
- V. Komolprasert, P. Turowski, *Food Law Compliance of Poly(ethylene Terephthalate) (PET) Food Packaging Materials* (ACS Symposium Series; American Chemical Society, 2014), vol. 1162.
- G. P. Karayannidis, D. S. Achilias, Chemical recycling of poly(ethylene terephthalate). *Macromol. Mater. Eng.* **292**, 128–146 (2007).
- D. Carta, G. Cao, C. D'Angeli, Chemical recycling of poly(ethylene terephthalate) (pet) by hydrolysis and glycolysis. *Environ. Sci. Pollut. Res.* **10**, 390–394 (2003).
- T. Yoshioka, T. Sato, A. Okuwaki, Hydrolysis of waste PET by sulfuric acid at 150°C for a chemical recycling. *J. Appl. Polym. Sci.* **52**, 1353–1355 (1994).
- H. P. Austin, M. D. Allen, B. S. Donohoe, N. A. Rorrer, F. L. Kearns, R. L. Silveira, B. C. Pollard, G. Dominick, R. Duman, K. El Omari, V. Mykhaylyk, A. Wagner, W. E. Michener, A. Amore, M. S. Skaf, M. F. Crowley, A. W. Thorne, C. W. Johnson, H. L. Woodcock, J. E. McGeehan, G. T. Beckham, Characterization and engineering of a plastic-degrading aromatic polyesterase. *Proc. Natl. Acad. Sci. U.S.A.* **115**, E4350–E4357 (2018).
- M. Genta, F. Yano, Y. Kondo, W. Matsubara, S. Oomoto, Development of chemical recycling process for post-consumer PET bottles by methanolysis in supercritical methanol. *Tech. Rev.* **40**, 1–4 (2003).
- S. Mishra, A. S. Goje, Kinetic and thermodynamic study of methanolysis of poly(ethylene terephthalate) waste powder. *Polym. Int.* **52**, 337–342 (2003).
- G. Güçlü, A. Kaşgöz, S. Özbudak, S. Özgümüş, M. Orbay, Glycolysis of poly (ethylene terephthalate) wastes in xylene. *J. Appl. Polym. Sci.* **69**, 2311–2319 (1998).
- K. Troev, G. Grancharov, R. Tsevi, I. Gitsov, A novel catalyst for the glycolysis of poly (ethylene terephthalate). *J. Appl. Polym. Sci.* **90**, 1148–1152 (2003).
- X. Zhang, M. Fevre, G. O. Jones, R. M. Waymouth, Catalysis as an enabling science for sustainable polymers. *Chem. Rev.* **118**, 839–885 (2018).
- EEA, “Circular economy to have considerable benefits, but challenges remain” (European Environment Agency, 2016).
- W. R. Stahel, The circular economy. *Nature* **531**, 435–438 (2016).
- B. Kiser, Circular economy: Getting the circulation going. *Nature* **531**, 443–446 (2016).
- E. M. Krall, T. W. Klein, R. J. Andersen, A. J. Nett, R. W. Glasgow, D. S. Reader, B. C. Dauphinais, Sean P. Mc Ilrath, A. A. Fischer, M. J. Camey, D. J. Hudson, N. J. Robertson,

- Controlled hydrogenative depolymerization of polyesters and polycarbonates catalyzed by ruthenium(II) PNN pincer complexes. *Chem. Commun.* **50**, 4884–4887 (2014).
17. E. Balaraman, B. Gnanaprakasam, C. Gunanathan, D. Milstein, J. Zhang, Novel ruthenium complexes and their uses in processes for formation and/or hydrogenation of esters, amides and derivatives thereof, U.S. Patent WO2012052996A2 (2013).
 18. E. Feghali, T. Cantat, Room temperature organocatalyzed reductive depolymerization of waste polyethers, polyesters, and polycarbonates. *ChemSusChem* **8**, 980–984 (2015).
 19. J. A. Fuentes, S. M. Smith, M. T. Scharbert, I. Carpenter, D. B. Cordes, A. M. Z. Slawin, M. L. Clarke, On the functional group tolerance of ester hydrogenation and polyester depolymerisation catalysed by ruthenium complexes of tridentate aminophosphine ligands. *Chemistry* **21**, 10851–10860 (2015).
 20. M. Meuresch, S. Westhues, W. Leitner, J. Klankermayer, Tailor-made ruthenium-triphos catalysts for the selective homogeneous hydrogenation of lactams. *Angew. Chem. Int. Ed. Engl.* **55**, 1392–1395 (2016).
 21. S. Westhues, M. Meuresch, J. Klankermayer, Ruthenium-catalyzed modular synthesis of cyclic tertiary amines from lactams. *Angew. Chem. Int. Ed. Engl.* **55**, 12841–12844 (2016).
 22. T. vom Stein, M. Meuresch, D. Limper, M. Schmitz, M. Hölscher, J. Coetzee, D. J. Cole-Hamilton, J. Klankermayer, W. Leitner, Highly versatile catalytic hydrogenation of carboxylic and carbonic acid derivatives using a Ru-triphos complex: Molecular control over selectivity and substrate scope. *J. Am. Chem. Soc.* **136**, 13217–13225 (2014).
 23. S. Li, M. Pignol, F. Gasc, M. Vert, Synthesis, characterization, and enzymatic degradation of copolymers prepared from ϵ -caprolactone and β -butyrolactone. *Macromolecules* **37**, 9798–9803 (2004).
 24. K. Thenert, K. Beydoun, J. Wiesenthal, W. Leitner, J. Klankermayer, Ruthenium-catalyzed synthesis of dialkoxymethane ethers utilizing carbon dioxide and molecular hydrogen. *Angew. Chem.* **128**, 12454–12457 (2016).
 25. B. G. Schieweck, J. Klankermayer, Tailor-made molecular cobalt catalyst system for the selective transformation of carbon dioxide to dialkoxymethane ethers. *Angew. Chem. Int. Ed. Engl.* **56**, 10854–10857 (2017).

Acknowledgments

Funding: This work was supported in part by the Cluster of Excellence “Tailor-Made Fuels from Biomass,” which is funded by the Excellence Initiative by the German Federal and State Governments to promote science and research at German universities, and by the German Federal Ministry of Education and Research within the Kopernikus Project P2X: Flexible use of renewable resources—Exploration, validation and implementation of “Power-to-X” concepts. Further, we are grateful for a gift of ruthenium precursor from Umicore AG.

Author contributions: S.W. and J.K. conceived the idea. S.W. and J.I. performed the experiments. S.W., J.I., and J.K. designed the experiments, analyzed the results, and wrote the manuscript. J.K. guided the research. **Competing interests:** The authors declare that they have no competing interests. **Data and materials availability:** All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 23 April 2018

Accepted 5 July 2018

Published 10 August 2018

10.1126/sciadv.aat9669

Citation: S. Westhues, J. Idel, J. Klankermayer, Molecular catalyst systems as key enablers for tailored polyesters and polycarbonate recycling concepts. *Sci. Adv.* **4**, eaat9669 (2018).

Molecular catalyst systems as key enablers for tailored polyesters and polycarbonate recycling concepts

Stefan Westhues, Jasmine Idel and Jürgen Klankermayer

Sci Adv 4 (8), eaat9669.
DOI: 10.1126/sciadv.aat9669

ARTICLE TOOLS

<http://advances.sciencemag.org/content/4/8/eaat9669>

SUPPLEMENTARY MATERIALS

<http://advances.sciencemag.org/content/suppl/2018/08/06/4.8.eaat9669.DC1>

REFERENCES

This article cites 22 articles, 2 of which you can access for free
<http://advances.sciencemag.org/content/4/8/eaat9669#BIBL>

PERMISSIONS

<http://www.sciencemag.org/help/reprints-and-permissions>

Use of this article is subject to the [Terms of Service](#)

Science Advances (ISSN 2375-2548) is published by the American Association for the Advancement of Science, 1200 New York Avenue NW, Washington, DC 20005. The title *Science Advances* is a registered trademark of AAAS.

Copyright © 2018 The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. No claim to original U.S. Government Works. Distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC).