Circularity in Mixed Plastics Chemical Recycling Enabled by Variable Rates of Polydiketoenamine Hydrolysis

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Abstract:

Footwear, carpet, soft furnishings, automotive interiors, and multi-layer packaging are examples of products manufactured from several types of polymers whose inextricability poses significant challenges for recycling at end-of-life. Here, we show that chemical circularity in mixed-polymer recycling becomes possible by controlling the rates of depolymerization of polydiketoenamines (PDKs) over several orders of magnitude through molecular engineering. Stepwise deconstruction of mixed-PDK composites, laminates, and assemblies is chemospecific, allowing a prescribed subset of monomers, fillers, and additives to be recovered in pristine condition at each stage of the recycling process. We provide a theoretical framework to understand PDK depolymerization via acid-catalyzed hydrolysis and experimentally validate trends predicted for the rate-limiting step. The control achieved by PDKs in managing thermal and materials entropy points to new opportunities for pairing circular design with sustainable manufacturing.

One Sentence Summary: Circularity in mixed-polymer recycling.

Polydiketoenamine variants address the challenge of recycling products made from several polymers to reusable feedstocks for sustainable manufacturing.

Main Text:

Products manufactured from two or more blended or laminated polymer resins are ubiquitous and present obstacles to chemical recycling due to the difficulty in and cost of deconstructing each polymer to their respective monomers for re-use in manufacturing supply chains (1–3). Recycling efforts are further challenged when such products also include metals or glass, e.g., as complex assemblies bonded together using adhesives or fixtures (4–6). The inability to recover valuable chemical and materials resources from these products at end-of-useful-life is both wasteful and unsustainable (7–12). Furthermore, the accumulation and leakage of non-recyclable mixed-polymer and mixed-material waste in the environment continues to strain global ecosystems (13–17).

Here, we show that chemospecificity in mixed-polymer recycling is achievable through molecular engineering of polydiketoenamines (PDKs) (18, 19) where fast- and slow-to-depolymerize PDK chemistries incorporated into either mixed-polymer or mixed-material products allow each PDK variant to be selectively deconstructed in space and time simply by varying the depolymerization temperature under acidic conditions (**Fig. 1a**). At each stage of a thermally-controlled recycling process, we recover specific monomers, additives, and fillers from PDK resins in either mixed-PDK blends, laminates, or assemblies that are indistinguishable from the associated primary feedstocks and re-usable in closed-loop materials lifecycles (**Fig. 1b,c**). The predictability and control afforded by PDKs in multi-stage chemical recycling suggest a common infrastructure may be used to recycle complex products that would normally be considered non-recyclable. Because specialized plastic recycling infrastructure is capital-intensive (20), a general process that handles a variety of materials—from polymers and thermosets to composites—could offer economic advantages and even enable recycling in industries that produce durable goods. If implemented, PDKs could relax a growing number of constraints faced by supply chain managers and product designers when making materials choices for circularity to meet their sustainability goals (21, 22)

to reduce the need for virgin resin. Pairing recycle-by-design chemistries with customer-focused take-back schemes is also poised to improve industrial materials efficiency.

Fig. 1. Closed-Loop chemical recycling of mixed-polymer waste. (A) Examples of consumer products featuring several polymer resins whose inextricability poses challenges to recycling at end-of-life for resource recovery. (B) Mixed-Polymer recycling can be realized if each polymer were to undergo chemical depolymerization at a different temperature, allowing specific monomers to be recovered in successive stages of the recycling process. These monomers may then be used in secondary polymer resin manufacturing processes to reduce the demand for primary chemical feedstocks. (C) Realization of mixed-polymer recycling with polydiketoenamines (PDKs), where molecular engineering of diketoenamine polymer bonds enables fine-control over polymerization rates in strong acid. Each PDK variant is deconstructed in a chemospecific manner simply by varying the depolymerization temperature.

Molecular-Engineering of triketone monomers yields structurally diverse PDK resins

PDKs are synthesized from polytopic triketone and amine monomers via spontaneous “click” polycondensation reactions (18, 19), which proceed under ambient conditions and do not require a promoter. The properties of PDKs are similar to those of nylons and polyurethanes, yet bridge those of plastics and thermosets due to their dynamic covalent character (18, 19, 23–26). While the formulation space for tailoring PDK properties is broad, resins formulated with structurally similar triketone monomers depolymerize at similar rates. For example, while changing the carbon chain length in triketone monomers used to synthesize PDK 1 resins changes their glass transition temperature and other characteristics (Fig. 2), it does not significantly change the rate of their chemical depolymerization to monomer, which is complete in ~12 h at 25 °C, or in ~1 h at 90 °C in 5.0 M H_2SO_4 or HCl (18). To differentiate the rates of PDK depolymerization, we designed PDKs 2–4, which vary in number and placement of heteroatoms relative to the keto functionality

in the ring (**Fig. 2a**). In doing so, we anticipated that their distinctive susceptibility for diketoenamine hydrolysis could give rise to orthogonal rates of PDK depolymerization, which would enable step-wise recovery of the embodied resources in mixed-PDK and mixed-material waste streams during chemical recycling.

In pursuit of this goal, we synthesized PDKs **1–4** from a cohesive group of ditopic triketone monomers **1–4** and *tris*(2-aminoethyl)amine (TREN) (**Fig. 2a**). As evidenced from single crystal X-ray diffraction (XRD) data (**Fig. 2b**), the preferred tautomer of triketone monomers **2–4** features an exocyclic enol, whereas that for triketone **1** features an endocyclic enol. Furthermore, the degree of asymmetry in hydrogen bonding highlights notable differences in electronegativity for *O*-centered hydrogen-bond acceptors and donors, with triketones **1** and **4** showing significant yet opposite asymmetries in hydrogen bonding by comparison to the more symmetric triketone **2** (**Tables S1–5**). Despite these differences, a common and unifying structure for the diketoenamine bond in all PDK resins is evident in XRD data of small molecule analogues (**Fig. S1** and **Table S6**) (18). PDKs **1–4** obtained after ball-mill polymerization were micron-sized dispersible powders (**Fig. S2**) and therefore suitable for pelletization or molding (**Fig. 2c**). Differential scanning calorimetry showed glass transition temperatures (T_g) of 96, 98, 104, and 136 °C for PDKs **1–4** (**Figs. S3–6**), respectively, with only slight variations in modulus (E') in either the glassy state (1.8–2.1 GPa) or rubbery state (5.3–6.9 MPa) as determined by dynamic mechanical analysis (**Table S7**).

Fig. 2. Molecularly-Engineered PDKs are depolymerized selectively and iteratively at different temperatures. (A) Triketone monomers **1–4** and their use in the chemical synthesis of PDKs **1–4** by polycondensation with *tris*(2-aminoethyl)amine (TREN). (B) Single-crystal X-ray structures for triketones **1–4** show distinctive packing in the solid-state and structure-dependent

hydrogen-bond symmetry and preferred tautomer. (C) Compression-molded samples of PDKs 1–4. (D) Chemospecific recycling of PDKs 1–4 to triketone and TREN monomers in 5.0 M HCl at 0, 20, 40, and 60 °C. Triketone monomers are recovered in pristine quality from PDKs 1, 2, and 4 (Figs. S7–10) and in high yield; recovery of triketone 3 was lower due to transformation of some of its chain ends to β -keto acids.

PDK variants depolymerize to monomer at different temperatures

To assess the rates of chemical depolymerization of PDKs 1–4, we dispersed the resin powders in strong acid (e.g., 5.0 M aqueous HCl) for up to 24 h at either 0, 20, 40, or 60 °C (Fig. 2d). PDK 1 was exclusively depolymerized at 0 °C to monomer (92% recovery), whereas PDK 2 was depolymerized at 20 °C to monomer with 99% recovery. Elevated temperature was required to depolymerize PDK 3 (51% recovery at 40 °C) and PDK 4 (88% recovery at 60 °C). Notably, while triketones 1, 2, and 4 were recovered from their corresponding PDKs in pristine condition (i.e., indistinguishable from the monomer used in primary resin production), triketone 3 showed signs of transformation to a β -keto acid in strong acid at elevated temperature (Figs. S7–10). In all cases, TREN can be recovered quantitatively from the filtrate after neutralization with a basic ion-exchange resin (18). Together, these data confirmed our hypothesis that varying the structure and electronics of the diketoenamine could enable variable rates of PDK depolymerization to monomer. The data further suggest that chemically recycling mixtures of resins is possible, permitting the recovery of two or more triketone monomers from TREN in consecutive yet fully closed-loops (Fig. 1).

Torsional strain dictates activation barrier to diketoenamine hydrolysis in strong acid

To understand the contrasting rates of PDK depolymerization to monomer, we carried out DFT simulations of the reaction coordinates for acid-catalyzed hydrolysis of small molecule diketoenamines 1–4 (Fig. 3 and Figs. S11–13), which represent the cleavable bonds in PDKs 1–4, respectively. Hydrolysis proceeds by an addition–elimination mechanism and features transition states corresponding to the addition of water to the acid-activated diketoenamine and the collapse of the tetrahedral hemiaminal to eliminate an alkylammonium and regenerate the triketone (Fig. 3a). We modeled all reactions in a continuum solvent from an initial state consisting of a hydronium ion and a reactive diketoenamine, whose *N,N*-dimethylaminoethyl moiety was protonated as it would be in strong acid. We optimized all molecular geometries using the m06-2X/6-311++G(2df,2p)/SMD level of theory (27, 28) and calculated free energies with the *quasi*-RRHO model (Table S8) (29). We found that protonation of the diketoenamine triggers the formation of an iminium, which rotates out-of-plane in advance of the addition of water in the rate-limiting step. Notably, the calculated standard free energies of activation ($\Delta G^\ddagger$) for the addition of water to the iminium vary by as much as 18 kJ mol^{−1} between diketoenamine variants (Fig. 3a) and trends are consistent with the observed differences in rates of depolymerization. We also found that differences in $\Delta G^\ddagger$ are highly dependent on the energy barrier associated with rotating the iminium into the transition state geometry. Specifically, potential energy barriers for rotation (E_{tor}) of the iminium dihedral display the same trend as $\Delta G^\ddagger$ across diketoenamines 1–4 (Fig. 3b).

Fig. 3. Molecular basis for the rate-limiting step in PDK hydrolysis. (A) Calculated energy landscapes along reaction coordinates for hydrolysis of PDKs 1–4 via an addition–elimination mechanism. Diketoenamines 1–4 are studied as surrogates of the bonds in PDKs 1–4 undergoing hydrolysis to triketones in acid. Intermediates along the reaction coordinate are shown for diketoenamine 2; reaction coordinates for hydrolysis of diketoenamines 1, 3, and 4 are given in **Figs. S11–13**. (B) Relative potential energy barriers (E_{tor}) for rotating the iminium out of plane to allow the addition of water in the transition state. (C) Experimentally determined rates of hydrolysis of diketoenamines 1–4 in 5.0 M DCl in D_2O at $T = 20^\circ\text{C}$; data are normalized to the hydrolysis rate for diketoenamine 4. Kinetic data at different temperatures and associated Eyring analyses are given in **Figs. S14–S17** and **Table S9**.

To experimentally benchmark the theoretical studies of the rate-limiting step for diketoenamine hydrolysis, we measured $\Delta G^\ddagger$ for acid-catalyzed hydrolysis of small molecule diketoenamines 1–4, which we synthesized from the corresponding triketones and *N,N*-dimethylethylenediamine. We dissolved diketoenamines 1–4 in 5.0 DCl in D_2O and monitored their hydrolysis to insoluble

triketones and soluble amine salts using variable temperature ^1H NMR spectroscopy (**Figs. S14–S17**). The relative rates of diketoenamine hydrolysis at 20 °C vary by over two orders of magnitude, with diketoenamines **1** and **2** hydrolyzing >150-times and >25-times faster than diketoenamine **4**, respectively (**Fig. 3c**). Furthermore, our calculated values for $\Delta G^\ddagger$ for the rate-limiting step in diketoenamine hydrolysis after Eyring analyses of the kinetics data agree well with both theoretical determinations (**Table S9**) and the observed temperature-dependent rates of PDK depolymerization as solid or molded resins (**Figs. 1 & 2**). We found that hydrolysis of diketoenamine **3** and ultimately depolymerization of PDK **3** were outliers in that their hydrolysis is faster than what is predicted by our DFT simulations. This discrepancy is explained by the apparent faster rate diketoenamine conversion when there is concurrent hydrolysis and degradation by decarboxylation to β -keto acids (**Fig. S18**), as evidenced by ^1H NMR (**Fig. S9**). Nevertheless, the convergence of computational and experimental data provide valid and important insights into the mechanism of diketoenamine hydrolysis and the underlying foundations for varying the rate of hydrolysis by molecular engineering of the diketoenamine bond through targeted heteroatom placement. These modifications unlock orthogonal rates of PDK polymerization, which can be put to use in multi-polymer and multi-material recycling, where there are few options to do so with polymers in use today.

Mixed-Polymer and mixed-material recycling enabled by chemospecific PDK deconstruction

To showcase emerging opportunities afforded by molecularly engineered PDKs **1–4** in mixed-polymer and mixed-material chemical recycling to monomer, we considered deconstructing an intimate blend of PDKs **1** and **4**, which are prepared as resin powders $\sim\mu\text{m}$ in size (**Fig. S2**). We mechanically mixed and molded the two PDK resin powders into a solid bar. We then carried out chemospecific depolymerization of PDKs **1** and **4** in two stages: initially at 20 °C endeavoring to depolymerize PDK **1** and then at 60 °C to depolymerize PDK **4** (**Fig. 4a**). After the first stage, we used simple solid–liquid separations to isolate triketone **1** and TREN monomers from intact PDK **4**. After the second stage, we isolated triketone **4** from TREN. Notably, only the prescribed set of monomers were isolated at each stage. We neither observed triketone **4** impurities in triketone **1** recovered in the first stage, nor did we observe triketone **1** impurities in triketone **4** recovered in the second stage. We found that this chemospecificity in mixed-PDK recycling extended to bilayer laminates, where pigments added to one of the resins (in this case, carbon black loaded into PDK **4**) could also be dissociated from the monomers (**Fig. 4b**).

Based on our success in deconstructing bilayer laminates, we further considered the deconstruction of a trilayer assembly of polypropylene (PP) and polyethylene terephthalate (PET) film featuring PDK **1** as an adhesive bonding layer. This architecture is a model system for flexible packaging, where the adhesive bonding layer is typically polyethylene or nylon, which complicates the recycling of multi-layer laminates due to difficulties in debonding the layers for sorting into homogeneous waste streams. Within 24 h at 20 °C, we found that the PDK **1** adhesive bonding layer was completely depolymerized, despite its low contact surface area with the acidic depolymerization medium. This allowed both PP and PET films to be separated and sorted (**Fig. 4c**). We also recovered monomers from PDK **1** without contamination, e.g., from any oligomers or monomers that may have depolymerized from PET in acid.

Figure 4. Chemical Circularity in Mixed-PDK and Mixed-Polymer Recycling. (A) A blend of PDK 1 and 4 resin powders was compression molded into a solid bar sample. At 20 °C in strong acid, PDK 1 was chemospecifically depolymerized into triketone monomer 1 and TREN; PDK 4 remained intact and was isolated as a solid. The isolated PDK 4 resin was then depolymerized at 60 °C to recover triketone monomer 4 and TREN. (B) A bilayer laminate of PDK 1 and carbon-black loaded PDK 4 was chemospecifically deconstructed to prescribed monomers in two stages, initially at 20 °C and then at 60 °C. (C) A trilayer laminate consisting of polypropylene (PP) film and poly(ethylene terephthalate) (PET) film laminated by PDK 1 was deconstructed as a model for recycling mixed-polymer, multi-layer packaging. (A–C) In all cases, recovered monomers showed indistinguishable characteristics from initial monomers, demonstrating chemical circularity in mixed-PDK and mixed-polymer recycling.

The orthogonality in PDK depolymerization at different temperatures makes possible the removal or recovery of essentially an endless series of additives compounded into the various PDK resins. As proof-of-concept, we compounded a blue pigment in PDK 2 and carbon black in PDK 4 to highlight that de-coloration and additive dissociation can be conducted concurrently at each stage of the recycling process (Fig. 5a). Despite chemical differences in the two pigments and an increase in number of solid–liquid separations processes, monomer recovery was high: 90% for triketone 2, and 75% for triketone 4. Both monomers were recovered with indistinguishable properties from those used in primary PDK resin production, thus completing the loop in chemical circularity for mixed-polymers and composites (Fig. S19 & S20).

To extend our purview of chemical circularity in mixed-material recycling with PDKs 1–4, we fabricated a bonded assembly comprising metal (stainless steel comprising mainly of Fe with ~12% Cr, ~0.6% C, and the remainder trace elements), glass, and PDKs 1 and 4; an epoxy resin was used to glue the assembly together. This assembly is a crude yet illustrative model for difficult-to-recycle products, from electronics to complex parts integrated into vehicles, aircraft, and

buildings (e.g., panels and windows). The challenge in mixed materials recycling is that the conditions used to depolymerize either PDK resin may affect the integrity of the metals and glass through corrosion or etching, respectively. Indeed, when PDK **1** was depolymerized from the bonded assembly at 20 °C in strong acid, the reaction mixture evidenced signs of metal corrosion, even at this low temperature. Despite this, we recovered triketone **1** free from metal and other impurities, as evidenced by both ^1H NMR (**Fig. S21**) and ICP-OES analysis, which is notable, given the propensity for some triketones to coordinate metals (30). After depolymerization PDK **1**, we then deconstructed the remainder of the assembly at 60 °C in strong acid, isolating metal from glass and separating triketone **4** from TREN using solid–liquid separations. For recovered triketone **4**, its ^1H NMR indicated high purity (**Fig. S22**); however, its slight coloration was tied to 2.85 ppm Fe and 0.19 ppm Cr, as quantified by ICP-OES. While metal contamination in triketone **4** remains lower by nearly two orders of magnitude by comparison to metal contamination of mechanically recycled polymers and slightly lower than virgin resins for commodity plastics (31), it can be refined to pristine metal-free quality by recrystallization.

Figure 5. Chemical Circularity in Deconstructing Multi-Color Composites and Bonded Multi-Material Assemblies. (A) Mixed-PDK composite recycling with de-coloration at each step was demonstrated by first depolymerizing blue dye-loaded PDK **2** at 20 °C in strong acid into triketone **2**, TREN, and a blue dye (whose hue is pH dependent). Carbon-Black loaded PDK **4** was then retrieved and separately depolymerized at 60 °C in strong acid to recover triketone **4** from TREN and carbon black, after filtration (filter shown). (B) Mixed-Material and Mixed-PDK recycling, where compression molded samples of PDK **1** and carbon-black loaded PDK **4** were glued to glass and metal sheets by an epoxy adhesive. PDK **1** was depolymerized at 20 °C to recover triketone **1** in pristine condition, which is notable given the contamination of the reaction mixture by metal corrosion. To deconstruct the metal–PDK **4**–glass bonded assembly, the temperature of the strongly acidic solution was raised to 60 °C to depolymerize PDK **4** and recover triketone monomer **4**. The presence of an adhesive did not appear to affect the yield or purity of recovered monomers from either PDK **1** or PDK **4**.

Conclusion

The outcomes demonstrated here address outstanding challenges in monomer-to-monomer chemical recycling for both mixed-polymer and mixed-material waste, which require additive- and impurity-tolerant chemical depolymerization and separation processes that are not universally available. Consequently, re-use strategies have instead focused on mixed-polymer upcycling, where mixtures of polymers are blended into a higher value material by compatibilization (32–34). However, products made from compatibilized polymer blends are difficult to sort at materials recovery facilities and more often contaminate sorted recycling streams. Furthermore, individual components within compatibilized blends undergo degradation by various forms of chain scission, suggesting limited re-use opportunities for polymer blends beyond the initial upcycle (35, 36). Sequential depolymerization of several polymers in complex mixtures is an attractive alternative, allowing re-use of monomer feedstocks, which significantly lowers greenhouse gas emissions by comparison to those generated in primary resin production (37, 38). However, it is rare for each of the polymers in mixed-polymer waste to be depolymerized sequentially to their respective monomers in high yield and purity (1, 2, 18, 39, 40), which we show here becomes possible when using PDK variants. In this way, PDKs provide an important entry point to managing thermal and materials entropy in circular manufacturing systems (41). In early applications, we expect industries that retain ownership of their assets or implement take-back programs will be most capable of using PDKs in closed-loop recycling. For example, in automotive manufacturing, where polymers and composites comprise nearly 10% of the weight an average vehicle, chemical circularity could provide a step-change in industrial materials efficiency as car-makers transition to mobility as a service (5, 6). Long term, we anticipate that collecting and sorting mixed-PDK waste in municipal recycling facilities will benefit from emerging digital barcoding strategies (42), which can be used to direct chemical recycling processes efficiently for resource recovery for a more sustainable and circular economy of polymers.

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Supplementary Materials:

Materials and Methods

Figures S1-S22

Tables S1-S9

References (43–55)

Materials and Methods

5,5-dimethyl-1,3-cyclohexanedione (dimedone, 95%), 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid, 95%), 1,3-dimethylbarbituric acid (>99%), sebacoyl chloride (>95%), 4-(dimethylamino)pyridine (DMAP, 99%), *N,N'*-dicyclohexylcarbodiimide (DCC, 99%), *N,N*-dimethylethylenediamine (95%), tris(2-aminoethyl)amine (TREN, 96%), magnesium sulfate (MgSO₄, anhydrous), potassium carbonate (K₂CO₃, >) and hydrochloric acid (HCl) were purchased from Sigma Aldrich and used as received. Carbon black (Super P® Conductive, 99%) was purchased from Alfa Aesar. Bio-based sebacic acid (99%) was purchased from Arkema. Triketone **1** was synthesized as described by us previously (18). All solvents—dichloromethane (DCM) (>99.9%), chloroform (CHCl₃) (>99.8%), ethyl acetate (>99.8%), hexane (>98.5%), acetone (>99.5%), pyridine (99%), acetonitrile (>99.8%), trifluoroacetic acid (>99.8%), formic acid (98–100%), ethanol (>99.5%)—were purchased from VWR and used without further purification. *N,N*-dimethylacetamide (>99%) was purchased from Sigma Aldrich and used without further purification. Dihydro-6,6-dimethyl-2*H*-pyran-2,4(3*H*)-dione (43), 2-acetyl-5,5-dimethyl-1,3-cyclohexanedione (18), 3-acetyl-6,6-dimethyldihydro-2*H*-pyran-2,4(3*H*)-dione (44), 5-acetyl-2,2-dimethyl-1,3-dioxane-4,6-dione (45), and 5-acetyl-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (46) were synthesized according to previously reported procedures. Biaxially-Oriented Poly(propylene) (BOPP) and Poly(ethylene terephthalate) (PET) foils were both purchased from Amazon. Loctite HY 4090 structural hybrid adhesive was purchased from Henkel.

¹H and ¹³C Nuclear Magnetic Resonance Spectroscopy was carried out using a Bruker Avance II at 500 MHz and 125 MHz, respectively. Chemical shifts are reported in δ (ppm) relative to the residual solvent peak: 1) CDCl₃: 7.26 for ¹H, 77.16 for ¹³C, or 2) D₂O: 4.8 for the hydrolysis kinetics in D₂O/DCI 5.0 M. Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet).

Electrospray Ionization Mass Spectrometry (ESI-MS) was carried out using a Bruker microTOF-Q using acetonitrile containing either 0.1% trifluoroacetic acid or 0.1% formic acid as the ionization medium.

Fourier Transform Infrared Spectra (FTIR). Data were acquired using a Perkin Elmer Spectrum One spectrophotometer as an average of 16 scans over an energy range of 400–4000 cm⁻¹.

Single Crystal XRD. Single crystals for triketones **1–4** were selected, mounted on Mitegen® loops with Paratone oil, and placed in an Oxford Cryosystems Cryostream 800 plus at *T* = 100 K. Data were collected on beamline 12.2.1 at the Advanced Light Source (Berkeley, CA) with λ = 0.7288 Å using a Bruker D8 diffractometer with a Bruker PHOTONII CPAD detector. Data reduction were performed and corrected for Lorentz and polarization effects using SAINT (47) v8.40a and were corrected for absorption effects and other effects using TWINABS 2012/1 (48) for triketones **1**, **3**, and **4**, while SADABS v2016/2 (49) was used for triketone **2**. Structure solutions were performed by SHELXT (50) using the direct method and were refined by least-square refinement against *F*² by SHELXL (51).

Differential Scanning Calorimetry (DSC). Data were acquired using a TA Instruments Q200 Differential Scanning Calorimeter. Samples were heated over a temperature range of either 40–220 °C (for PDKs **1**, **2** & **4**) or 40–120 °C (for PDK **3**) at a rate of 5 °C min⁻¹ under a N₂ atmosphere. For each sample, data acquisition runs consisted of a heating step, a cooling step, and a second heating step. Glass transition temperatures (T_g) were interpreted and reported from the second heating curve with the exception of PDK **3**, those T_g was interpreted from the first heating curve due to decomposition.

Dynamic Mechanical Analysis (DMA). Data were acquired using a TA instruments DMA Q800 in tensile mode. All samples were fabricated as rectangular specimens with ~ 0.5 mm (T) $\times$ 5 mm (W) $\times$ 20 mm (L). Each sample was tested at a frequency of 1 Hz with a displacement amplitude of 15 μ m and a preload force of 0.01 N. Heating ramps of 3 °C min⁻¹ were applied from 40–200 °C. The softening temperature was reported as the maximum value of $\tan \delta$.

Scanning Electron Microscopy (SEM). Imaging was performed using a Zeiss Gemini Ultra-55 Analytical Field Emission Scanning Electron Microscope with a 5 kV accelerating voltage and using the secondary detector mode. Polymer powders were deposited onto carbon tape affixed to the stainless steel stage in the microscope. Excess polymer was removed using a stream of compressed air and the sample was sputter-coated with gold (thickness ~ 7 nm) prior to analysis by SEM.

Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). Concentrations of Fe and Cr in parts per million (ppm) in triketones **1** and **4**, chemically recycled using strong acid from mixed-material waste containing stainless steel, were quantified by ICP-OES 720ES (Varian) equipped with an axial argon torch. For each determination, ~ 10 mg of triketone was oxidatively digested at ambient temperature in concentrated HNO₃ (~ 200 μ L) at ambient temperature for 24 h and subsequently diluted with MilliQ water to 10 mL in a precision volumetric flask prior to analysis and comparison to a calibration curve for each element.

Theoretical Methods. All calculations were performed using Gaussian 16 (52). For the reaction pathway free energy calculations, the computational model included the small molecule and one explicit hydronium ion encased in a continuum dielectric medium using the SMD implicit solvent model (53). To identify the global minimum energy conformers for each step of the reaction pathway, we performed a random rotor conformer search for each structure. For each structure with n rotors, 3^n conformers were generated by rotating each rotor twice in 120° increments. We then selected 200 conformers randomly, optimized the geometry of each structure and compared the energies at the b97d/6-31g(d,p) level of theory in vacuum. We then identified the lowest energy conformer by optimizing the geometry of the 10 lowest energy structures from the initial search and comparing the energies at the m062x/6-31+g(d,p)//SMD level of theory. For transition state structures, the bond distance of the primary bond being broken or formed at the transition state was constrained during the conformer search. In addition, we compared the lowest-energy structures of each diketoenamine to the others and evaluated additional conformers based on substitution of those structures. We then performed a final geometry optimization and free energy calculation at the m062x/6-311++g(2df,2p)//SMD level of theory. For steps 1 and 2 in the reaction pathway, in which there were two molecules in the system, calculations were performed separately for each fragment. We also employed Grimme's Quasi-RRHO free energy model to correct for

inaccurate vibrational entropy contributions from low-frequency modes as calculated in Gaussian16 with a pure harmonic oscillator model (54). Free energies were calculated at 298K and corrected for the standard state of liquid water,

$$G_{sol} = G_{\text{Quasi-RRHO}} + RT\ln([\text{H}_2\text{O}]).$$

To calculate the dihedral torsion potentials, the dihedral angle was constrained in 10° increments beginning with the structure in step 2 of the reaction pathway. We performed a constrained geometry optimization for each dihedral angle at the m062x/6-311++g(d,p)//SMD level of theory.

Supplementary Text

Synthesis of 3,3'-(1,10-dihydroxydecane-1,10-diyl)bis(6,6-dimethyldihydro-2H-pyran-2,4(3H)-dione) (Triketone 2).

Dihydro-6,6-dimethyl-2H-pyran-2,4(3H)-dione (4.00 g, 28.2 mmol), sebacic acid (2.83 g, 14.0 mmol), and DMAP (5.13 g, 42.0 mmol) were dissolved in dichloromethane ([dihydro-6,6-dimethyl-2H-pyran-2,4(3H)-dione] = 1.0 M) with stirring. A separate solution of DCC (6.94 g, 33.6 mmol) in dichloromethane ([DCC] = 1.0 M) was added slowly at room temperature to the reaction mixture. The pale-yellow solution gradually turned darker yellow, which was accompanied by the formation of a white precipitate. The mixture was stirred at room temperature overnight (16 h), at which point the white *N,N'*-dicyclohexylurea precipitate was filtered. The precipitate was washed with DCM until colorless. The filtrate was collected and washed with 3% HCl until the pH of the aqueous phase was < 3. The organic phase was separated, dried over MgSO₄, filtered and the solvent is removed under vacuum. The crude, pale yellow solid was solubilized in 300 mL K₂CO₃ (1.0 M) and the mixture stirred for 2 h, filtered, and precipitated in 500 mL HCl (1.0 M). The mixture was filtered and the colorless solid dried under vacuum overnight (84% isolated yield). A small amount of the purified solid was recrystallized from ethanol to yield colorless needles for single crystal XRD. Characterization Data: ¹H NMR (500 MHz, CDCl₃): δ 17.97 (s, 2H), 16.28 (s, 2H), 3.02–3.05 (t, ³J_{H-H} = 7.35 Hz, 4H), 2.70 (s, 4H), 2.63 (s, 4H), 1.62–1.66 (m, 4H), 1.47 (s, 12H), 1.32–1.36 (m, 10H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ 204.00, 197.06, 195.09, 190.09, 174.48, 163.60, 102.74, 100.05, 79.51, 76.60, 49.45, 44.18, 38.44, 36.22, 33.52, 29.42, 29.24, 29.19, 29.12, 29.00, 27.67, 27.42, 26.05, 25.03 ppm; ESI-MS: *m/z* for (C₂₄H₃₄O₈)₂Na⁺ ([2M+Na]⁺) calculated 923.4400, found 923.4684. FT-IR: 2975, 2939, 2869, 2856, 1691, 1549, 1467, 1454, 1415, 1402, 1385, 1371, 1318, 1287, 1265, 1228, 1212, 1175, 1126, 1059, 1005, 988, 938, 907, 850, 837, 771, 721, 643, 603, 540, 506, 483, 433 cm⁻¹.

¹H NMR of TK 2.

¹³C NMR of TK 2.

FT-IR of TK 2.

Synthesis of 5,5'-decanediylbis(2,2-dimethyl-1,3-dioxane-4,6-dione) (Triketone 3).

Meldrum's acid (5.00 g, 34.7 mmol) was dissolved in pyridine (25 mL) with stirring at room temperature to form a light-yellow homogenous solution, which was protected from light. The solution was cooled to 0 °C prior to the slow addition of sebacoyl chloride (4.04 g, 16.9 mmol). The orange reaction mixture was stirred at 0 °C for another 1 h, and the pH was then adjusted to < 3 by 1.0 M HCl at 0 °C. The yellow precipitate formed was collected by filtration and washed with 1.0 M HCl. The precipitate was re-dissolved in DCM and further washed with 1.0 M HCl (1 x 20 mL) and brine (1 x 20 mL). The organic phase was separated, dried over MgSO₄, filtered and the solvent is removed under vacuum to yield pale yellow solid as the crude product (75% isolated yield). The crude product was recrystallized in acetone/hexane to yield colorless needles. Characterization Data: ¹H NMR (500 MHz, CDCl₃): δ 15.29 (s, 2H), 3.04–3.07 (t, ³J_{H-H} = 7.35 Hz, 4H), 1.58–1.73 (m, 16H), 1.34–1.40 (m, 4H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ 198.24, 170.59, 160.24, 104.82, 91.24, 35.73, 29.27, 28.99, 26.82, 26.06 ppm; ESI-MS: *m/z* for (C₂₂H₃₀O₁₀)₂Na⁺ ([2M+Na]⁺) calculated 931.3570, found 931.3695. FT-IR: 3000, 2939, 2925, 2859, 1725, 1642, 1574, 1466, 1458, 1423, 1399, 1390, 1383, 1342, 1294, 1280, 1263, 1242, 1231, 1203, 1151, 1062, 1053, 1035, 1014, 955, 916, 893, 847, 798, 731, 721, 643, 605, 548, 506, 496, 458, 410 cm⁻¹.

¹H NMR of TK 3.

¹³C NMR of TK 3.

FT-IR of TK 3.

Synthesis of 5,5'-(1,10-dihydroxydecane-1,10-diylidene)bis(1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione) (Triketone 4).

1,3-dimethylbarbituric acid (100 g, 640.5 mmol) was dissolved in pyridine (220 mL) and DMF (50 mL) with stirring at room temperature to give a light-yellow homogenous solution. A solution of sebacoyl chloride (74.7 g, 312.4 mmol) in DMF (50 mL) was added dropwise, which was accompanied by the formation of a precipitate. The mixture was stirred at room temperature during 4 h, at which point the white precipitate was filtered. The precipitate was washed with DMF until colorless. The crude solid was recrystallized from *N,N*-dimethylacetamide to yield colorless needles (85% isolated yield). Characterization Data: ^1H NMR (500 MHz, CDCl_3): δ 17.53 (s, 2H), 3.37 (s, 6H) 3.33 (s, 6H), 3.10–3.14 (t, $^3J_{\text{H-H}} = 7.60$ Hz, 4H), 1.65–1.71 (m, 4H), 1.33–1.42 (m, 8H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 199.84, 169.78, 160.86, 150.40, 95.22, 36.73, 29.37, 29.10, 28.03, 27.83, 25.79 ppm; ESI-MS: m/z for $\text{C}_{22}\text{H}_{30}\text{N}_4\text{O}_8\text{Na}^+$ ($[\text{M}+\text{Na}]^+$) calculated 501.1961, found 501.1818. FT-IR: 2935, 2868, 1719, 1664, 1552, 1492, 1473, 1446, 1360, 1269, 1225, 1201, 1044, 1005, 994, 948, 877, 841, 787, 754, 730, 713, 672, 568, 503, 483, 421, 403 cm^{-1} .

¹H NMR of TK 4.

¹³C NMR of TK 4.

FT-IR of TK 4.

General Procedure for the Synthesis of Diketoenamines 1–4. To any of the acetyl-diones 1–4 (1.00 mmol) in CHCl_3 (4 mL) was added *N,N*-dimethylethylenediamine (1.00 mmol). The reaction mixture was stirred for 2 h at ambient temperature, after which the volatiles were removed under reduced pressure and the crude product was purified via a silica plug from 9:1 EtOAc:MeOH (v/v) to obtain the respective diketoenamines 1–4.

2-(1-((2-(dimethylamino)ethyl)amino)ethylidene)-5,5-dimethylcyclohexane-1,3-dione (DKE 1).

Isolated as brown oil (76% yield). Characterization data: ^1H NMR (500 MHz, CDCl_3): δ 13.36 (br s, 1H), 3.44–3.48 (td, $^3J_{\text{H-H}} = 6.20$ Hz, 5.10 Hz, 2H), 2.56–2.59 (t, 2H, $^3J_{\text{H-H}} = 6.35$ Hz), 2.56 (s, 3H), 2.36 (br s, 4H), 2.30 (s, 6H), 1.02 (s, 6H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 197.35, 173.21, 107.95, 57.39, 52.87, 45.29, 41.40, 30.08, 28.28, 18.25 ppm; ESI-MS: m/z for $(\text{C}_{14}\text{H}_{24}\text{N}_2\text{O}_2)_2\text{H}^+$ ($[2\text{M}+\text{H}]^+$) calculated 505.3748, found 505.4131. FT-IR: 3454, 2953, 2867, 2822, 2770, 1634, 1567, 1458, 1420, 1385, 1367, 1323, 1300, 1285, 1210, 1184, 1142, 1125, 1099, 1039, 948, 879, 821, 786, 728, 624, 585, 541, 512, 463 cm^{-1} .

¹H NMR of DKE **1**.

¹³C NMR of DKE **1**.

3-(1-((2-(dimethylamino)ethyl)amino)ethylidene)-6,6-dimethyldihydro-2H-pyran-2,4(3H)-dione (DKE 2).

Isolated as pale yellow solid (83% yield) consisting of two regioisomers in 1:4.5 ratio. Characterization data: ^1H NMR (500 MHz, CDCl_3): δ 12.96 (s, 1H, major), 11.82 (s, 1H, minor), 3.45–3.48 (td, major, $^3J_{\text{H-H}} = 5.95$ Hz, 5.40 Hz, 2H), 2.56–2.58 (t, major, $^3J_{\text{H-H}} = 6.20$ Hz, 3H), 2.55 (s, 2H, major), 2.54 (s, 2H, major), 2.31 (s, 6H, major), 1.41 (s, 6H, major) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 193.47, 191.16, 173.20, 172.35, 170.75, 166.98, 97.02, 95.37, 75.63, 57.33, 49.64, 48.19, 41.82, 27.46, 18.07 ppm; ESI-MS: m/z for $(\text{C}_{13}\text{H}_{22}\text{N}_2\text{O}_3)_2\text{H}^+$ ($[2\text{M}+\text{H}]^+$) calculated 509.3334, found 509. FT-IR: 3250, 3066, 2974, 2947, 2859, 2818, 2765, 1679, 1652, 1617, 1594, 1563, 1443, 1412, 1384, 1375, 1370, 1334, 1272, 1235, 1201, 1175, 1159, 1123, 1098, 1071, 1055, 1038, 993, 951, 928, 858, 841, 786, 772, 727, 651, 632, 595, 578, 561, 523, 481, 427 cm^{-1} .

¹H NMR of **DKE 2**.

¹³C NMR of **DKE 2**.

FT-IR of DKE 2.

5-(1-((2-(dimethylamino)ethyl)amino)ethylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (DKE 3).

Isolated as a pale yellow solid (68% yield). Characterization data: ^1H NMR (500 MHz, CDCl_3): δ 11.46 (br s, 1H), 3.46–3.49 (td, $^3J_{\text{H-H}} = 6.20$ Hz, 5.10 Hz, 2H), 2.62 (s, 3H), 2.57–2.60 (t, $^3J_{\text{H-H}} = 6.25$ Hz, 2H), 2.30 (s, 6H), 1.67 (s, 6H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 173.20, 167.09, 163.44, 102.30, 84.44, 57.18, 45.28, 41.95, 26.40, 18.22 ppm; ESI-MS: m/z for $(\text{C}_{12}\text{H}_{20}\text{N}_2\text{O}_4)_2\text{H}^+$ ($[\text{2M}+\text{H}]^+$) calculated 513.2919, found 513.3124. FT-IR: 3100, 2998, 2983, 2943, 2859, 2820, 2793, 2766, 2728, 1712, 1698, 1652, 1576, 1459, 1422, 1394, 1387, 1375, 1322, 1296, 1267, 1204, 1166, 1095, 1069, 1045, 1039, 1015, 988, 955, 927, 890, 866, 832, 791, 738, 720, 648, 583, 570, 531, 518, 510, 448 cm^{-1} .

¹H NMR of DKE **3**.

¹³C NMR of DKE **3**.

FT-IR of DKE 3.

5-(1-((2-(dimethylamino)ethyl)amino)ethylidene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (DKE 4).

Isolated as a pale pink solid (74% yield). Characterization data: ^1H NMR (500 MHz, CDCl_3): δ 12.55 (br s, 1H), 3.49–3.52 (td, $^3J_{\text{H-H}} = 6.20$ Hz, 5.10 Hz, 2H), 3.32 (s, 3H), 3.30 (s, 3H), 2.70 (s, 3H), 2.58–2.61 (t, $^3J_{\text{H-H}} = 6.25$ Hz, 2H), 2.31 (s, 6H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 173.78, 166.20, 163.13, 151.48, 90.43, 57.51, 45.42, 41.99, 27.86, 27.65, 18.28 ppm; ESI-MS m/z for $(\text{C}_{12}\text{H}_{20}\text{N}_4\text{O}_3)_2\text{H}^+$ ($[2\text{M}+\text{H}]^+$) calculated 537.3144, found 537.2999. FT-IR: 3588, 3588, 2949, 2856, 2815, 2758, 1701, 1642, 1613, 1578, 1462, 1409, 1346, 1298, 1276, 1257, 1218, 1167, 1093, 1037, 989, 946, 916, 852, 783, 774, 754, 741, 687, 574, 555, 501, 467 cm^{-1} .

¹H NMR of DKE 4.

¹³C NMR of DKE 4.

FT-IR of DKE 4.

PDK Polymerization by Ball-Milling. Ball-milling was performed using a Retsch Planetary Ball-Mill PM100. The container in which the reactions were carried out was a zirconium-coated cylinder either with an inner diameter of 4.5 cm and a height of 3.5 cm (reactor volume ~50 mL) or with an inner diameter of 10 cm and a height of 7 cm (reactor volume ~500 mL). All experiments reported herein used the same weight of zirconium oxide ball bearings (5 mm diameter) and triketone ratio, being 10 times the weight of triketone. The general procedure for all ball-milling reactions involved weighing out the appropriate amount of ditopic triketone monomer (2.0 or 10.0 g) and placing the powder at the bottom of the ball mill, along with the ball bearings (20 or 100 g). To the triketone monomer was added *tris*(2-aminoethyl)amine (TREN) using a pre-calibrated micropipette, which was immediately followed by ball-milling the contents of the closed container for 30 min at a rotation of 500 rpm. The reactor was opened to air and the reactor walls were scraped to bring together the reactants homogeneously. Ball-milling was resumed for an additional 30 min under the same rotation speed. The powder was recovered from the reactor and the residual water removed under vacuum.

FT-IR of PDK 1.

FT-IR: 3450, 2927, 2861, 1633, 1561, 1465, 1420, 1385, 1366, 1333, 1286, 1141, 1123, 1098, 1054, 1032, 1012, 883, 720, 681, 624, 570, 521, 464, 418 cm^{-1} .

FT-IR of PDK 2.

FT-IR: 2973, 2926, 2853, 1658, 1585, 1467, 1385, 1326, 1295, 1263, 1226, 1174, 1120, 1090, 1047, 992, 943, 840, 770, 726, 676, 632, 595, 542, 484, 430 cm^{-1} .

FT-IR of PDK 3.

FT-IR: 2992, 2926, 2854, 1702, 1629, 1464, 1430, 1382, 1332, 1295, 1263, 1203, 1157, 1087, 1022, 950, 793, 743, 670, 645, 559, 512, 451, 409 cm⁻¹.

FT-IR of PDK 4.

FT-IR: 2924, 2852, 1692, 1588, 1409, 1379, 1232, 1086, 998, 866, 781, 757, 665, 511, 483, 415 cm⁻¹.

Compounding PDKs with Additives or Fillers. Composites were prepared by ball-milling for 1 min at a rotation of 500 rpm PDK resin powders with 0–1% w/w filler (carbon black or Disperse Blue dye).

Preparation of solid samples for hydrolysis and DMA. Powdered materials obtained from the ball-mill were pressed into sheets of ~ 1 mm in thickness using a thermal press operating at 100 °C for PDK 1 and PDK 2 and at 140 °C for PDK 4, at 20k psi for 20 min. Small rectangular samples both used for hydrolysis kinetics and DMA were shaped with dimensions of $l = 20$ mm, $w = 5$ mm, $t = 1$ mm. Larger rectangular samples for multi-material hydrolysis experiments were shaped with dimensions of $l = 35$ mm, $w = 25$ mm, $t = 1$ mm. Gel fractions for compression molded PDKs, after swelling the specimens for 24 h at 90 °C in DMF, were 90–100%.

Acid-Catalyzed Hydrolytic Depolymerization of PDKs 1–4. PDK resin powders 1–4 (~500 mg) were each placed in a 40 mL vial containing strong acid (5.0 M HCl, 10 mL) and a magnetic stirrer. Depolymerization reactions were conducted over a 24 h at either 0, 20, 40, or 60 °C.

Powdered PDK 1 (500 mg) was completely depolymerized at 60 °C in aqueous 5.0 M HCl (10 mL) over 48 h, yielding a white precipitate, which was isolated by centrifugation and rinsed with water. The solid was solubilized in K₂CO₃ (2.0 M, 10 mL), the filtrate was precipitated in HCl (2.0 M, 30 mL), and the TK 1 precipitate was filtrated and dried under vacuum (yield 371 mg, 92%).

Powdered PDK 2 (500 mg) was completely depolymerized at 20 °C in aqueous 5.0 M HCl (10 mL) over 24 h, yielding a yellow precipitate, which was isolated by filtration. The solid was solubilized in aqueous 2.0 M K₂CO₃ (10 mL), the yellow filtrate was precipitated in HCl (2.0 M, 30 mL), and the TK 2 precipitate was recovered by filtration and dried under vacuum (yield 402 mg, 99%).

Powdered PDK 3 (500 mg) was completely depolymerized at 40 °C in aqueous 5.0 M HCl (10 mL) over 24 h, yielding a brown precipitate, which was extracted with DCM (2 x 10 mL). The solvent was evaporated under vacuum and the brown powder was dried under vacuum. ¹H NMR analysis revealed a mixture of TK 3 (yield_{NMR} = 51%) and β-keto acids.

Powdered PDK 4 (500 mg) was completely depolymerized at 60 °C in aqueous 5.0 M HCl (10 mL) over 24 h, yielding a yellow precipitate, which was extracted with DCM (2 x 10 mL). The solvent was evaporated under vacuum and the yellow-white powder was triturated with fresh portions of water (2 x 10 mL). The mixture was centrifuged, the liquid was removed and the TK 4 monomer was dried under vacuum (yield 360 mg, 88%).

Tortoise Material Chemical Recycling of PDKs. Powdered PDK 1 was pressed using a stainless-steel mold at 100 °C at 20 kpsi during 20 min to reach a homogeneous yellow rectangle. Small squares with dimensions of $l = 5$ mm and $w = 5$ mm were cut from this yellow PDK 1 rectangle. Similarly, powdered PDK 4 containing 1% of carbon black was pressed at 140 °C at 20 kpsi during 20 min to reach a homogeneous black rectangle. Small squares with dimensions of $l = 5$ mm and $w = 5$ mm were cut from this black PDK 4 rectangle.

The mixed-PDK tortoise assembly was poured in aqueous 5.0 M HCl (15 mL) and depolymerized during a 48 h 20 °C isotherm into a white precipitate and untouched black PDK 4 squares. The

white mixture was centrifuged and once the acid liquid removed, aqueous 2.0 M K_2CO_3 (10 mL) was poured over the solid mixture to solubilize TK 1 monomer. Basic TK 1 solution was extracted and precipitated in HCl (2.0 M, 30 mL), the TK 1 precipitate was recovered by filtration and dried under vacuum for ^1H NMR analysis.

^1H NMR of pristine and recycled TK 1 from tortoise material.

The PDK 4 square-shaped chips were rinsed with water and transferred in a 20 mL vial containing 15 mL of fresh 5.0 M HCl. The depolymerization was pursued 72 h at 60 °C, after which, a fine black precipitate appeared. The TK 4 monomer was extracted from the aqueous mixture with DCM (2 x 10 mL) and filtrated on paper to remove residual carbon black. The organic phase was isolated and the solvent evaporated under vacuum. The yellow precipitate was triturated with water (10 mL), then centrifuged and dried under vacuum for ^1H NMR analysis.

^1H NMR of pristine and recycled TK 4 from tortoise material.

Molecular Blend Chemical Recycling of PDKs. Powdered PDK **1** (1000 mg) and PDK **4** (250 mg) were mixed in a vial and were pressed at 140 °C at 20 kpsi during 20 min to reach a homogeneous yellow rectangle. The PDK blend was shaped with dimensions of $l = 35$ mm, $w = 10$ mm, $t = 1$ mm. The solid PDK blend (551 mg) was poured in aqueous 5.0 M HCl (15 mL) and depolymerized during a 24 h 20 °C isotherm into a yellow precipitate that was isolated by centrifugation. Aqueous 2.0 M K₂CO₃ (10 mL) was poured over the solid mixture to solubilize TK **1** monomer while white PDK **4** powder was centrifuged and isolated for further recycling. Basic TK **1** solution was extracted and precipitated in HCl (2.0 M, 30 mL), the TK **1** precipitate was recovered by filtration and dried under vacuum for ¹H NMR analysis.

¹H NMR of pristine and recycled TK **1** from molecular blend material.

Centrifuged PDK **4** powder was poured in aqueous 5.0 M HCl (10 mL) and depolymerized during a 72 h 60 °C isotherm into a yellow precipitate, which was extracted with DCM (2 x 10 mL). The solvent was evaporated under vacuum and the yellow-white powder was triturated with fresh portions of water (2 x 10 mL). The mixture was centrifuged, the liquid was removed and the TK **4** monomer was dried under vacuum for ¹H NMR analysis.

¹H NMR of pristine and recycled TK **4** from molecular blend material.

Bilayer Laminate Chemical Recycling of PDKs. Powdered PDK **1** (~700 mg) was pressed using a stainless-steel mold at 100 °C at 20 kpsi during 20 min to reach a homogeneous yellow rectangle. Powdered PDK **4** containing 1% of carbon black (~500 mg) was then added over the yellow rectangle and was pressed at 140 °C at 20 kpsi during 20 min to reach a homogeneous bilayer black and yellow rectangle. The rectangle was shaped with dimensions of $l = 35$ mm, $w = 10$ mm, $t = 1$ mm. The solid bilaminate PDK was poured in aqueous 5.0 M HCl (15 mL) and depolymerized during a 24 h 20 °C isotherm into a yellow precipitate that was isolated by centrifugation. Aqueous 2.0 M K₂CO₃ (10 mL) was poured over the solid mixture to solubilize TK **1** monomer while black PDK **4** solid pieces were centrifuged, isolated and dried under vacuum. Basic TK **1** solution was extracted and precipitated in HCl (2.0 M, 30 mL), the TK **1** precipitate was recovered by filtration and dried under vacuum for ¹H NMR analysis.

¹H NMR of pristine and recycled TK **1** from bilayer laminate material.

The carbon black-loaded PDK **4** sample was rinsed with water and transferred in a 20 mL vial containing 10 mL of fresh 5.0 M HCl. Depolymerization was conducted over 72 h at 60 °C, after which, a fine black precipitate appeared. The TK **4** monomer was extracted from the aqueous mixture with DCM (2 x 10 mL) and filtrated on paper to remove residual carbon black. The organic phase was isolated and the solvent evaporated under vacuum. The yellow precipitate was triturated with water (10 mL), then centrifuged and dried under vacuum for ¹H NMR analysis.

^1H NMR of pristine and recycled TK 4 from bilayer laminate material.

Acid-Catalyzed Hydrolytic Depolymerization of Laminate made of Biaxially-Oriented Poly(propylene) (BOPP)/PDK 1/Poly(ethylene terephthalate) (PET). Commercially available BOPP (0.05 mm thick) and PET (0.2 mm thick) were used as external layers of the laminate. PDK 1 powder was pressed at 140 °C at 20 kpsi during 20 min to reach a homogeneous yellow transparent layer (0.4 mm thick). Then, BOPP/PDK 1/PET layers were pressed into a unique laminate foil at 140 °C at 60 psi. The laminate was cut into a rectangle of 2 cm long and 1 cm large. The latter was transferred in a 20 mL vial containing 10 mL of 5.0 M HCl. The depolymerization was conducted over 48 h at room temperature, after which, a fine precipitate remained in suspension, while colorless transparent BOPP and PET foils remained untouched. The precipitate was filtered, washed with water to remove residual acid and then solubilized in 2.0 M K_2CO_3 (5 mL) for 10 min, followed filtering of residual solids and slowly precipitating a white solid out of excess 2.0 M HCl (10 mL), maintaining a $\text{pH} < 3$. The yellow precipitate (TK 1) was collected by filtration, washed with water and dried under vacuum for ^1H NMR analysis.

^1H NMR of pristine and recycled TK 1 from laminate packaging material.

Multi-Polymer Recycling via Thermally Controlled Sequential Acid-Catalyzed Hydrolytic Depolymerization of PDKs 2 and 4 and Monomer Recovery from Additives and Fillers.

Powdered PDK 2 (1.20 g) and PDK 4 (1.20 g) were separately ball-milled with 0.1% (w/w) disperse blue 3 and 1% (w/w) carbon black respectively, using 10 g of zirconium oxide bearings in 50 mL reactor during 5 min to yield a green PDK 2 powder and a black PDK 4 powder. The powdered green and black polymer samples were pressed separately during 20 min 20k psi into two solid pieces at 100 °C for PDK 2 and 140 °C for PDK 4. Each sample was then cut to dimensions of ~2 cm² and 1 mm thick ($m_{\text{PDK 2}} = 397$ mg and $m_{\text{PDK 4}} = 503$ mg) and placed in a unique 20 mL vial containing aqueous 5.0 M HCl (15 mL). The depolymerization proceeded 24 h at room temperature, after which, a fine precipitate remained in suspension of a red mixture, while black PDK 4 sample remained untouched. The precipitate was filtered, washed with water to remove residual acid and then stirred in 2.0 M K₂CO₃ (10 mL) for 10 min, followed filtering of residual solids and slowly precipitating a white solid out of excess 2.0 M HCl (30 mL), maintaining a pH < 3. The yellow precipitate (TK 2) was collected by filtration, washed with water, and dried under vacuum (yield 286 mg, 90%).

The carbon black-loaded PDK 4 sample was rinsed with water and transferred in a 20 mL vial containing 15 mL of fresh 5.0 M HCl. The depolymerization was pursued 72 h at 60 °C, after which, a fine black precipitate appeared. The TK 4 monomer was extracted from the aqueous mixture with DCM (2 x 10 mL) and filtrated on paper to remove residual carbon black. The organic phase was isolated and the solvent evaporated under vacuum. The yellow precipitate was triturated with water (10 mL), then centrifuged and dried under vacuum (yield 307 mg, 75%).

Carbon black was recovered from the aqueous phase by centrifugation and filtration and was dried under vacuum.

Multi-Material Chemical Recycling of PDKs with Metal and Glass. Powdered PDK 1 was pressed using a stainless-steel mold at 100 °C at 20 kpsi during 20 min to reach a homogeneous yellow rectangle. Similarly, powdered PDK 4 containing 1% of Carbon Black was pressed at 140 °C at 20 kpsi during 20 min to reach a homogeneous black rectangle. The multi-material was constructed using a metal blade and a rectangular-shaped glass with structural hybrid adhesive layers as binder: metal/adhesive/PDK 4/adhesive/glass/adhesive/PDK 1.

The multi-material assembly was poured in aqueous 5.0 M HCl (25 mL) and depolymerized during a 24 h 20 °C isotherm into a white precipitate in light-green liquid. PDK 1 was selectively deconstructed under these conditions while the rest of the multi-material remained linked. The green mixture was centrifuged and once the acid liquid removed, aqueous 2.0 M K₂CO₃ (10 mL) was poured over the solid mixture to solubilize TK 1 monomer. Basic TK 1 solution was extracted and precipitated in HCl (2.0 M, 30 mL), the TK 1 precipitate was recovered by filtration and dried under vacuum for ¹H NMR analysis.

The metal/adhesive/PDK 4/adhesive/glass/adhesive assembly was rinsed with water and transferred in a 40 mL vial containing 20 mL of fresh 5.0 M HCl. The depolymerization was pursued 72 h at 60 °C, after which, a fine black precipitate appeared in dark-green liquid. The TK 4 monomer was extracted from the aqueous mixture with DCM (2 x 10 mL) and filtrated on paper to remove residual carbon black. The organic phase was isolated and the solvent evaporated under

vacuum. The yellow precipitate was triturated with water (10 mL), then centrifuged and dried under vacuum for ^1H NMR analysis.

Hydrolysis Studies of Diketoenamines 1–4. At a determined temperature, preliminary lock, tune, shim and run of the initial DKE spectra were realized before the kinetics runs. The DKE (5 mg) was solubilized in 600 μL of 5.0 M $\text{D}_2\text{O}/\text{DCl}$ and transferred in a sealed-cap NMR tube. The NMR tube was introduced to the preheated NMR and spectra were subsequently acquired at different preset time intervals. Conversion values were calculated using the signal at 2.32 ppm (t, 2H, - NCH_2CH_2 -) and the 2 CH_3 signal of the cyclic part of the DKE molecule. The procedure was repeated at different temperatures.

Integration of the enamine peak in the ^1H NMR spectrum was used to calculate the disappearance of the diketoenamine starting material. The first-order rate law,

$$\ln\left(\frac{[\text{diketoenamine}]_0}{[\text{diketoenamine}]}\right) = k_{\text{obs}} * t,$$

was then used to calculate k_{obs} .

Based on this equation, k_{obs} could be calculated at 20 $^\circ\text{C}$ for each DKE molecule, which enables the calculation of relative k_{obs} .

$\Delta G^\ddagger$ was determined using the Eyring equation (55):

$$\ln(k_{\text{obs}}/T) = \frac{\Delta H^\ddagger}{RT} + \ln \frac{k_B}{h} + \frac{\Delta S^\ddagger}{R}$$

From the extraction of $\Delta H^\ddagger$ and $\Delta S^\ddagger$, $\Delta G^\ddagger$ was calculated via the $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$.

Figure S1. Single Crystal X-Ray structure for DKE **3**. Legend: Carbon (black), Nitrogen (blue) Oxygen (red) and Hydrogen (open circles).

Figure S2. SEM image of PDK **1** resin powder.

Figure S3. DSC of ball-milled PDK **1** resin powder.

Figure S4. DSC of ball-milled PDK 2 resin powder.

Figure S5. DSC of ball-milled PDK **3** resin powder. First heating curve shown, as this resin showed signs of thermal decomposition during the experiment.

Figure S6. DSC of ball-milled PDK 4 resin powder.

Figure S7. ^1H NMR of pristine and recycled TK **1** from PDK **1** resin powder.

Figure S8. ^1H NMR of pristine and recycled TK 2 from PDK 2 resin powder.

Figure S9. ^1H NMR of pristine TK 3, recycled TK 3, and the bis(β -keto acid) byproduct isolated from depolymerizing PDK 3 resin powder.

Figure S10. ^1H NMR of pristine and recycled TK 4 from PDK 4 resin powder.

Figure S11. Computed free energy pathway of DKE **1** hydrolysis.

Figure S12. Computed free energy pathway of DKE 3 hydrolysis.

Figure S13. Computed free energy pathway of DKE **4** hydrolysis.

Figure S14. Hydrolysis kinetics of DKE 1 at 20, 30, and 40 °C.

Figure S15. Hydrolysis kinetics of DKE 2 at 30, 40, and 50 °C.

Figure S16. Hydrolysis kinetics of DKE 3 at 45, 55, and 65 °C.

Figure S17. Hydrolysis kinetics of DKE 4 at 60, 70, and 80 °C.

Figure S18. Competing pathways in the reactivity of DKE **3** at elevated temperature in strong acid, leading to an overestimation of the rate of hydrolysis when monitoring the rate of change in concentration of the starting material over time in small molecule kinetics studies.

Figure S19. ^1H NMR of pristine and recycled TK **2** from PDK **2** that had been compounded with a blue dye prior to orthogonal mixed-PDK recycling with PDK **4**.

Figure S20. ^1H NMR of pristine and recycled TK 4 from PDK 4 that had been compounded with carbon black prior to orthogonal mixed-PDK recycling with PDK 2.

Figure S21. ^1H NMR of pristine and recycled TK **1** from PDK **1**, after its selective depolymerization during mixed-material recycling with PDK **4**, stainless steel, and glass.

Figure S22. ^1H NMR of pristine and recycled TK 4 from PDK 4, after its selective depolymerization during mixed-material recycling with PDK 1, stainless steel, and glass.

Table S1.

Select O–H bond distances extracted from X-ray crystallography data for TKs **1–4**.

	d_{O2-H} (Å)	d_{H-O3} (Å)
TK 1	1.08 ± 0.02	1.38 ± 0.02
TK 2	1.32 ± 0.02	1.17 ± 0.02
TK 3	1.67 ± 0.02	0.88 ± 0.02
TK 4	1.44 ± 0.03	1.05 ± 0.03

Table S2.

Crystal data and structure refinement for TK 1.

Identification code	TK 1	
Empirical formula	C ₂₆ H ₃₈ O ₆	
Formula weight	446.56	
Temperature	100(2) K	
Wavelength	0.7288 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /n	
Unit cell dimensions	a = 7.3061(3) Å	a = 90°.
	b = 8.7123(3) Å	b = 98.5400(10)°.
	c = 18.5578(7) Å	g = 90°.
Volume	1168.16(8) Å ³	
Z	2	
Density (calculated)	1.270 Mg/m ³	
Absorption coefficient	0.093 mm ⁻¹	
F(000)	484	
Crystal size	0.200 x 0.180 x 0.100 mm ³	
Theta range for data collection	2.276 to 31.386°.	
Index ranges	-10 ≤ h ≤ 10, 0 ≤ k ≤ 12, 0 ≤ l ≤ 26	
Reflections collected	131132	
Independent reflections	3575 [R(int) = 0.0794]	
Completeness to theta = 25.930°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.991 and 0.943	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3575 / 0 / 153	
Goodness-of-fit on F ²	1.082	
Final R indices [I > 2σ(I)]	R1 = 0.0403, wR2 = 0.1125	
R indices (all data)	R1 = 0.0447, wR2 = 0.1154	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.486 and -0.220 e.Å ⁻³	

Table S3.

Crystal data and structure refinement for TK 2.

Identification code	TK 2	
Empirical formula	C ₂₄ H ₃₄ O ₈	
Formula weight	450.51	
Temperature	100(2) K	
Wavelength	0.7288 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.0669(3) Å b = 9.7745(4) Å c = 9.8331(4) Å	a = 113.8060(10)°. b = 103.456(2)°. g = 103.752(2)°.
Volume	560.83(4) Å ³	
Z	1	
Density (calculated)	1.334 Mg/m ³	
Absorption coefficient	0.104 mm ⁻¹	
F(000)	242	
Crystal size	0.100 x 0.060 x 0.005 mm ³	
Theta range for data collection	2.499 to 31.410°.	
Index ranges	-10 ≤ h ≤ 10, -13 ≤ k ≤ 13, -14 ≤ l ≤ 14	
Reflections collected	19224	
Independent reflections	3423 [R(int) = 0.0272]	
Completeness to theta = 25.930°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.999 and 0.913	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3423 / 0 / 151	
Goodness-of-fit on F ²	1.058	
Final R indices [I > 2σ(I)]	R1 = 0.0342, wR2 = 0.0972	
R indices (all data)	R1 = 0.0381, wR2 = 0.1007	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.419 and -0.221 e.Å ⁻³	

Table S4.

Crystal data and structure refinement for TK 3.

Identification code	TK 3	
Empirical formula	C ₂₂ H ₃₀ O ₁₀	
Formula weight	454.46	
Temperature	100(2) K	
Wavelength	0.7288 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 5.1711(3) Å	a = 78.101(2)°.
	b = 7.1213(4) Å	b = 81.767(2)°.
	c = 16.2442(10) Å	g = 69.228(2)°.
Volume	545.68(6) Å ³	
Z	1	
Density (calculated)	1.383 Mg/m ³	
Absorption coefficient	0.114 mm ⁻¹	
F(000)	242	
Crystal size	0.300 x 0.160 x 0.005 mm ³	
Theta range for data collection	2.636 to 31.438°.	
Index ranges	-7 ≤ h ≤ 7, -9 ≤ k ≤ 10, 0 ≤ l ≤ 23	
Reflections collected	20410	
Independent reflections	3339 [R(int) = 0.0421]	
Completeness to theta = 25.930°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.999 and 0.852	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3339 / 0 / 152	
Goodness-of-fit on F ²	1.106	
Final R indices [I > 2sigma(I)]	R1 = 0.0356, wR2 = 0.0968	
R indices (all data)	R1 = 0.0396, wR2 = 0.0992	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.280 and -0.223 e.Å ⁻³	

Table S5.

Crystal data and structure refinement for TK 4.

Identification code	TK 4	
Empirical formula	C ₂₂ H ₃₀ N ₄ O ₈	
Formula weight	478.50	
Temperature	100(2) K	
Wavelength	0.7288 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /n	
Unit cell dimensions	a = 4.0129(2) Å	a = 90°.
	b = 7.9565(3) Å	b = 92.196(2)°.
	c = 34.4436(14) Å	g = 90°.
Volume	1098.93(8) Å ³	
Z	2	
Density (calculated)	1.446 Mg/m ³	
Absorption coefficient	0.116 mm ⁻¹	
F(000)	508	
Crystal size	0.400 x 0.020 x 0.010 mm ³	
Theta range for data collection	2.694 to 29.114°.	
Index ranges	-5 ≤ h ≤ 5, 0 ≤ k ≤ 10, 0 ≤ l ≤ 45	
Reflections collected	22549	
Independent reflections	2746 [R(int) = 0.0777]	
Completeness to theta = 25.930°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.999 and 0.376	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2746 / 0 / 161	
Goodness-of-fit on F ²	1.087	
Final R indices [I > 2σ(I)]	R1 = 0.0511, wR2 = 0.1362	
R indices (all data)	R1 = 0.0536, wR2 = 0.1395	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.569 and -0.343 e.Å ⁻³	

Table S6. Crystal data and structure refinement for **DKE 3**.

Identification code	DKE 3	
Empirical formula	C₁₂ H₂₀ N₂ O₄	
Formula weight	256.30	
Temperature	100(2) K	
Wavelength	0.7288 Å	
Crystal system	Monoclinic	
Space group	P2₁/c	
Unit cell dimensions	a = 22.2450(10) Å	a = 90°.
	b = 12.2739(6) Å	b = 95.997(2)°.
	c = 10.0926(5) Å	g = 90°.
Volume	2740.5(2) Å³	
Z	8	
Density (calculated)	1.242 Mg/m³	
Absorption coefficient	0.098 mm⁻¹	
F(000)	1104	
Crystal size	0.050 x 0.020 x 0.005 mm³	
Theta range for data collection	2.542 to 26.131°.	
Index ranges	-26<=h<=26, -14<=k<=14, -12<=l<=12	
Reflections collected	60504	
Independent reflections	5034 [R(int) = 0.0743]	
Completeness to theta = 25.930°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.860	
Refinement method	Full-matrix least-squares on F²	
Data / restraints / parameters	5034 / 62 / 356	
Goodness-of-fit on F ²	1.067	
Final R indices [I>2sigma(I)]	R1 = 0.0447, wR2 = 0.1167	
R indices (all data)	R1 = 0.0549, wR2 = 0.1232	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.343 and -0.311 e.Å⁻³	

Table S7.

Summary of thermomechanical characterization data for PDKs **1**, **2** and **4** by dynamic mechanical analysis (DMA).

	Storage Modulus (GPa)	Elastic Modulus (MPa)
PDK 1	1.81	5.33
PDK 2	2.03	5.67
PDK 4	2.12	6.86

Table S8.

Calculated concentration-corrected Quasi-RRHO free energies for DKEs 1–4.

		G (Ha)			
		DKE 1	DKE 2	DKE 3	DKE 4
Step 1	DKE	−807.9513	−843.91132	−879.86946	−914.16442
	H ₃ O ⁺	−76.427354	−76.828115	−76.828115	−76.828115
Step 2	DKE	−808.37459	−844.32997	−880.27989	−914.57758
	H ₂ O	−76.427354	−76.427354	−76.427354	−76.427354
Step 3	DKE	−884.77008	−920.7224	−956.66857	−990.96997
Step 4	DKE	−884.78517	−920.74423	−956.66857	−990.99176
Step 5	DKE	−884.77007	−920.72422	−956.6725	−990.97172
Step 6	TK	−614.95734	−650.91452	−686.87091	−721.17064
	Amine	−269.85009	−269.85009	−269.85009	−269.85009

Table S9. Eyring analyses for the hydrolysis of DKEs **1–4** in 5.0 M DCl in D₂O.

	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	ΔG at 298 K (kJ mol ⁻¹)
DKE 1	77.9	3.9	76.8
DKE 2	79.2	−6.7	81.2
DKE 3	123.2	128.9	84.8
DKE 4	94.4	18.2	89.0

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