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Lower-Cost, Lower-Carbon Production of Circular Polydiketoenamine Plastics

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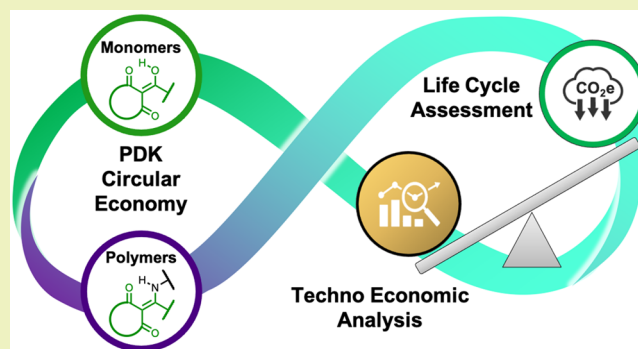
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Supporting Information

ABSTRACT: The efficiency by which monomers may be recovered during the chemical recycling of plastic waste has thus far dominated the discussion over which future polymer chemistries might be more sustainable than those in use today. However, at scale, other factors emerge as equally important, such as the costs of primary versus secondary resin production as well as the energy and carbon intensity of circular manufacturing processes. We apply systems analysis to identify problematic chemical processes used for the primary production of plastics designed for infinite recyclability: polydiketoenamine (PDK) resins from novel triketone and amine monomers. Leveraging this knowledge, we advance a less intensive process for triketone production, which lowers the cost of primary PDK production by 57% and results in 66% less life-cycle greenhouse gas (GHG) emissions. Using the automotive sector as a case study, we discuss the impact of replacing nonrecyclable polyurethane with circular PDK over the next 60 years. We find that the cumulative GHG emissions associated with introducing PDK are half those of staying the course with polyurethane. However, the extent to which circularity is realized through targeted collection and sorting plays the dominant role in determining how much of those savings is practically achievable.

KEYWORDS: plastic waste, chemical recycling, circular polymers, polydiketonamine, life-cycle assessment, technoeconomic analysis



INTRODUCTION

To decrease the volume of plastic waste entering landfills or leaking into the environment, circularity in plastics recycling has emerged as a priority.^{1,2} For example, the European Union (EU) has approved a 0.8 Euro (approximately 1 U.S. Dollar) tax per kilogram of virgin plastic resin in an effort to increase market demand for recycled material.³ Unfortunately, most widely used polymers are costly to recover and recycle with the currently available infrastructure. Mechanical recycling alone cannot eliminate the production and disposal of single-use plastic items, as noted in concerns raised about the difficulties in securing approval for mechanically recycled plastics in food contact materials (FCM).⁴ Improved recycling processes that enable the production of higher-quality recycled plastics than what is currently possible with mechanical recycling are essential to the broader strategy of reducing plastic waste accumulation in landfills and leakage into the environment. Chemical recycling of plastic waste can achieve this vision of increased circularity by depolymerizing polymer chains back to reusable monomers, which allows additives and fillers to be more readily dissociated from them. In doing so, the manufacturing and use history of plastics are erased. Monomers are recovered and refined for reuse in secondary

resin production without deterioration of resin properties, which is unavoidable with conventional mechanical recycling.

The ease and attractiveness of polymers for both conventional mechanical recycling and chemical recycling varies. Despite being the most commonly recycled plastic (17% recycle rate) and comprising 15% of total plastic use in the U.S.,⁵ polyethylene terephthalate (PET) has received a disproportionate share of the research aimed at developing novel recycling technologies.^{6,7} Conversely, polymers with considerably lower recycle rates (<5%) are in need of alternative solutions, in the form of either improved recycling processes and/or more easily recyclable replacements. Polyurethane (PU), for example, has been chemically recycled at commercial scale through acidolysis and glycolysis, both of which require clean foam as an input and produce only rigid polyols as reusable materials. Improved recycling processes are also under development for polyamide (nylon) fibers, such as

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those used in carpet; standard recycling processes require extensive cleaning and removal of unwanted contaminants. The challenges and costs associated with recycling PU and nylon to virgin-quality materials motivated the development of more recyclable alternatives with similar or advantaged properties.

On the other hand, polydiketoenamides (PDK) are an emerging family of polymers designed for infinite recyclability. Their properties are similar to PU and nylon and may be suitable replacements in some applications. PDK polymers, and other vitrimers, are unique in that they exhibit characteristics of both thermoplastics and thermosets as a result of their dynamic bonding, which is well-documented and unique to dynamic covalent polymer networks.^{8–10} Although additional testing is required to confirm the substitutability of PDK for PU or nylon in specific applications, the similarity in properties between PDK and PU is evidenced by previously published data on the tensile strength (stress at break) of PDK elastomers, which ranges from 18 to 31 MPa, falling within the range of commercially available polyurethane rubbers (0.6–44.1 MPa).^{11,12} As applied to PDK resins, the term infinitely recyclable refers to the ability to recover virgin-quality monomers at comparatively high yields (90–99%, depending on formulation) relative to other chemical recycling strategies. PDK resins are produced from commercially available amine monomers as well as novel triketones, which are synthesized from 1,3-diketones and dicarboxylic acids.^{11,13–15} By combining technoeconomic analysis (TEA), life-cycle greenhouse gas (GHG) modeling, and further process development for the production of PDKs, we highlight the key cost and emission drivers and explore the degree to which the minimum selling price (MSP) and GHG footprint can be reduced. We also discuss the implications of PDK circularity in the automotive market segment, where reductions in automotive shredder residue (ASR) in landfills has emerged as a priority given the widespread use of plastics in vehicle lightweighting.

MATERIALS AND METHODS

Materials. 5,5-Dimethyl-1,3-cyclohexanedione (dimeone, Sigma–Supelco, 99%), 4-(dimethylamino)pyridine (DMAP, Sigma, >99%), sebacoyl chloride (Sigma, >95%), anhydrous aluminum chloride (AlCl₃, Sigma, 99.99%), sodium sulfate decahydrate (Na₂SO₄·10H₂O, Sigma, >99%), Celite 535 (Sigma), potassium carbonate (K₂CO₃, Sigma, >98%), ethyl acetate (Fisher, 99%), pyridine (Fisher, 99%), dichloromethane (Fisher, 99%), and toluene (Fisher, 99%) were all used as received. Deionized water was used for extraction processes.

Methods. Detailed procedures for chemical synthesis and characterization are given in the [Supporting Information](#).

MODELING

Process Design and Technoeconomic Analysis. We used TEA to estimate the minimum selling price (MSP) for PDK resins. We use the term resin to refer to the processable material at its highest density (where densification has occurred via extrusion–pelletization or molding after synthesis and compounding). The terms PDK and PDK resin are interchangeable for this analysis. The MSP represents a selling price at which the cost of production and associated revenue balance out with a net present value equal to zero, including an internal rate of return. To estimate the MSP, we first combined experimental data with chemical process modeling, which provides mass and energy balances as well as equipment required for the hypothetical facility. Using an excel-based cash

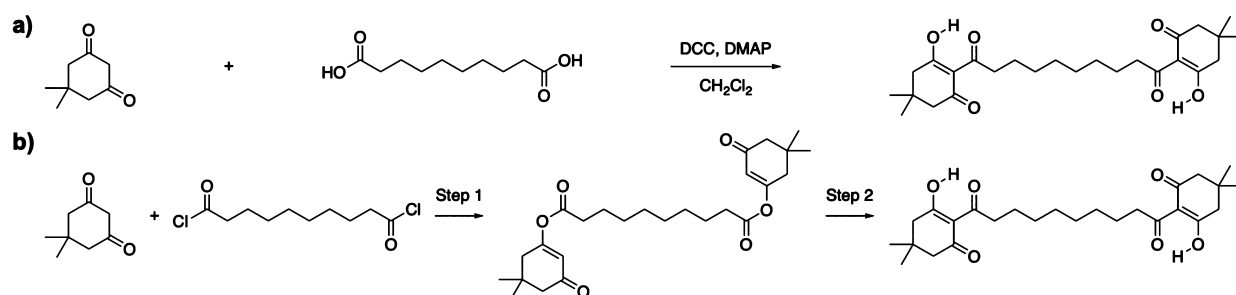
flow model, these outputs can be translated into the final minimum selling price for virgin PDK as well as recycled PDK.¹⁶ The process modeling was conducted in SuperPro Designer software.¹⁷ Diagrams and further details are included in the [Supporting Information](#) section entitled Process Models.

The facility was modeled to operate for 330 days per year and 24 h per day (equivalent to 90% uptime). We chose a facility scale of 20 000 t of PDK production per year, which is consistent with the assumption in Vora et al.¹⁵ and is based on typical recycling facility sizes as well as input from industry experts. Although a larger facility size would improve the economies of scale, it would also increase transportation distances and costs needed to collect sufficient waste PDK. Capital costs account for equipment purchase cost, installation costs, warehouse, site development, permits, land, and other field expenses and project contingency costs. Operation and maintenance costs account for costs of sourcing materials, facility, cost of labor, and cost of waste disposal. We assumed a discount rate of 10%, income tax rate of 35%, and the declining balance method for depreciation, consistent with U.S. Internal Revenue Service guidelines. These and other assumptions underpinning the TEA model are consistent with Humbird et al.¹⁸ and Vora et al.¹⁵ unless otherwise specified. All solid, water, and hazardous waste are treated offsite and were assigned a cost of disposal based on U.S. Environmental Protection Agency's average disposal pricing data.¹⁹ We modeled an onsite combined heat and power unit that relies on natural gas. Any excess energy is sold to the grid for a credit based on average U.S. electricity prices. We treated all solvents as hazardous waste as per the Resource Conservation and Recovery Act (RCRA) requirements. If the outgoing stream contained 10% or more of any individual solvents, or a mixture, it was deemed hazardous waste.²⁰ Our modeling relies on an assumed 95% solvent recovery rate. While solvent recovery and recycling increases the facility's on-site energy consumption, the cost associated with hazardous waste management is reduced by maximizing solvent recycling. Because our process model does not account for potential waste heat recovery, our energy use modeling estimates represent an upper bound and are conservative in nature. In future work, conducting pinch analysis and optimizing for heat exchange units can further reduce the energy footprint of solvent recycling.

The input and output stream data are provided in the [Table S2](#). The bulk prices for material costs were obtained from peer-reviewed literature, market price reports, and Alibaba, as documented in Vora et al.¹⁵ and [Table S3](#). When bulk pricing data were not available (e.g., sebacoyl chloride), we leveraged guidance from industry experts and used estimated yields, synthesis stoichiometry, and reactant prices to estimate the price. The estimation method, along with pricing estimates, are provided in the [SI](#). Equipment prices were derived from built-in pricing estimates in SuperPro. As material prices can fluctuate, we use sensitivity analysis to capture this variation. We apply a 20% variation to factors contributing a high percentage of price identified in the baseline case ([Table S3](#)).

Life Cycle Assessment. The goal of this LCA is to gauge recent progress and inform the further development of lower-cost, lower-carbon PDKs. The study also aims to compare PDKs with PUs, based on an assumption that the two materials can be functionally equivalent in an automotive application. First, the study compares the original PDK production process with the updated DCC-free chemistry. Because the two products are expected to be functionally equivalent, we do

Scheme 1. Chemical Routes for Triketone Monomer Production: (a) DCC-Based, Conducted in One Step, and (b) DCC-Free, Conducted over One or Two Steps



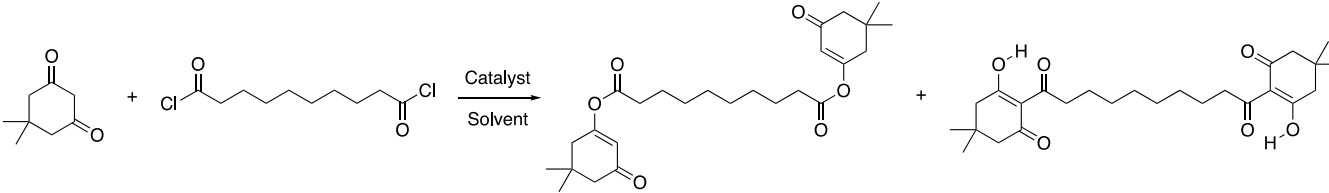
not model use-phase emissions as those would be identical between the two products. The system boundary for the analysis of primary PDK resin production is cradle-to-gate. To incorporate the comparison of virgin PDK with circular PDK, however, recovery of waste material and transport to recycling facilities is required. These processes are incorporated into the analysis of circular PDK, as further detailed by Vora et al.¹⁵ For both virgin and circular PDK, the functional unit for the analysis is 1 kg of PDK produced (virgin or recycled). We used a hybrid LCA approach combining material and energy balances from the process model (for the process-based component of the LCA model) with a physical units-based input–output approach to estimate indirect upstream impacts from production of raw materials and fuels. Further details on the underlying assumptions are available in previously published work.^{21,22} Life-cycle inventory data and characterization factors for input materials and commodity polymers were obtained from peer-reviewed literature,^{15,23,24} EcoProfiles, and LCA databases including Ecoinvent,²⁵ US Life Cycle Inventory (USLCI), GREET,²⁶ and WARM²⁷ models. As noted in the TEA section, we model on-site heat and electricity generation using natural gas and assume excess (if any) will be sold to the grid. We use the U.S. average electricity grid mix for emissions credits. As our primary goal is to generate sufficient electricity and heat for the synthesis, we optimize for this by only generating what is theoretically required to meet both electricity and heat needs. While marginal excess electricity is generated (Table S1) and is assumed to be sold to the grid, it is small compared to total electricity use in the upstream supply chain, and this results in a net positive electricity use as shown in Figure 3. We assumed that hazardous waste is incinerated and estimated the resulting GHG emissions based on IPCC waste incineration emissions calculation guidelines (Table S5).²⁸ LCA inventories were translated into the midpoint impact of 100-year global warming potential (GWP). Similar to the TEA, we used sensitivity analysis to estimate an optimistic and pessimistic scenario with best and worst possible cases. Where multiple data sources were available for specific emission factors, we used the range of values to establish upper and lower bounds. In cases where data availability was limited, we assumed an ad hoc 20% variation (Table S4).

Material Flow Modeling. In a previously published study, we found that the price of circular PDK can be comparable to virgin PET and high density polyethylene (HDPE) and lower than PU, assuming PDK can be recovered through product/packaging takeback systems.¹⁵ In the early stages of commercialization, a novel polymer like PDK is unlikely to make up a sufficiently large fraction of the municipal recycling

stream, meaning material recovery facilities would be unlikely to invest the space and capital equipment needed to recover PDK waste. In this study, we further focus on PU, end-use markets, and the potential for PDK to compete in similar segments. In 2019, the largest end-use sectors for PU were in building and construction (41% of total U.S. production), transportation (19%), and furniture and bedding (18%).²⁹ Here, we focus on PDK use in transportation and, in particular, the automotive industry. Growing sales³⁰ and commitments to transition to hybrid and electric vehicles³¹ combined with increasing interest in vehicle lightweighting make automotive industry an attractive segment to explore.³² Additionally, deploying and quickly transitioning to circular PDK resins will be more successful in a dedicated take-back system as opposed to a consumer waste recycling supply chain.¹⁵ In the U.S., more than 95% of vehicles are recycled at their end of life, making them one of the most recycled products in the U.S.³³ Currently, a majority of this recycling is focused on recovering metals and lead acid batteries; however, given E.U. directives and recent relaxation by the EPA on recycling auto shredder residue (currently used plastic ends up as shredder residue), there is a renewed interest in recovery of plastics.³³

We devised a simplified model for estimating cumulative GHG emissions and total waste diverted from landfill, if all PU (rigid and flexible) in transportation were replaced with PDK. We used log-normal distributions to model the year a light-vehicle reaches end of life, with a mean of 13 years and a standard deviation of 3, based on results from Geyer et al.³⁴ However, it is worth noting that vehicle automation and greater penetration of electric vehicles may affect stock turnover rates in the future.³⁵ In 2019, 0.6 million metric tons of PU was used in the transportation sector.²⁹ For the sake of comparison between PU and PDK, we assume that demand remains stable, and each year a consistent production of 0.6 million metric tons of resin occurs for the next 60 years. For PDK, the production begins with virgin materials and transitions to a mix of virgin PDK and recycled PDK, as more waste is recovered based on recycling rates when vehicles reach their end of life. In contrast, we assume all of the PU produced is landfilled as automotive shredder residue. For PDK, we make two simplified assumptions regarding the rate of material recovery for recycling: a low value of 44% recovery and an upper bound of 99%. The 44% projection is a linear extrapolation to 2050 based on results in Geyer et al.,³⁴ and the 99% upper bound reflects the recycling rate for lead acid batteries in the U.S.³⁶

Table 1. Screening of Catalyst, Base, and Solvent for a DCC-Free Triketone Monomer Production



entry ^a	catalyst	base	solvent	product (%) ^b		
				O-acyl	triketone	sebacic acid
1		pyridine	DCM	100 ^d	0	0
2	DMAP	NEt ₃	DCM	91	9	0
3 ^c				40	60	0
4	SmCl ₃	NEt ₃	DCM	100	0	0
5	MSA			15	0	85

^aConditions: $T = 20\text{ }^{\circ}\text{C}$, dropwise of sebacoyl chloride, DCM = dichloromethane, [dimedone] = 0.25 M, reaction time = 4 h, sebacoyl chloride conversion = 100%. ^bCalculated by ¹H NMR in CDCl₃ from the crude. ^cSame conditions as in entry 2, except with reaction time = 24 h. ^dIsolated yield = 83%

RESULTS AND DISCUSSION

In a prior life-cycle assessment (LCA) and techno-economic analysis (TEA) of PDK, we identified the chemical process for triketone production as the major contributor to cost, energy use, and GHG emissions.¹⁵ In the discovery phase, we synthesized triketone monomers via chemical condensation of 1,3-diketones and dicarboxylic acids, using *N,N'*-dicyclohexylcarbodiimide (DCC) as the dehydrating agent and 4-(dimethylamino)pyridine (DMAP) to promote rapid *O*- to *C*-acyl rearrangement (Scheme 1a).¹³ We found that this reaction scales well. However, superstoichiometric quantities of DMAP were used, and the *N,N'*-dicyclohexylurea (DCU) byproduct of the reaction is a known immunosensitizer and therefore is classified as hazardous. Together, these substrates and reagents as well as the nature of the byproducts result in a MSP for PDK resin of $\sim\$45\text{ kg}^{-1}$ and 86 kg CO₂e per kg of PDK. DCC and DMAP together account for 54% of the cost and 57% of these emissions. To lower the barrier for market entry, it is therefore desirable to develop an alternative route to triketone monomers that improves upon the discovery-based chemistry.

To circumvent the use of DCC and a large excess of DMAP, we considered replacing the dicarboxylic acids with widely available diacid chlorides, which in principle could allow the direct conversion of those reagents to triketone monomers in the presence of a promoter. This strategy was inspired by the ease by which related triketones have been prepared from acid chlorides and either Meldrum's acid or *N,N'*-dialkylbarbituric acids under mildly basic conditions.³⁷

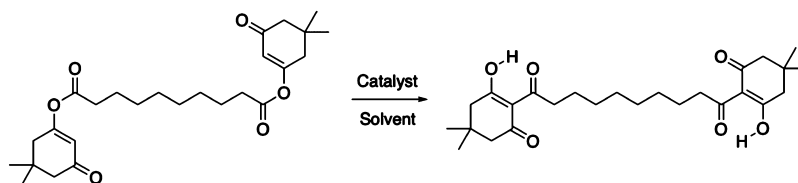
To test this strategy, we reacted sebacoyl chloride with dimedone (1 equiv) in dichloromethane in the presence of pyridine as a base (1.5 equiv), which produced an *O*-acylated product and not the desired *C*-acylated product (Table 1, entry 1). Thus, when dimedone is deprotonated, electronic effects appear to favor acylation at oxygen, whereas when Meldrum's acid or *N,N'*-dialkylbarbituric acids are deprotonated, electronic effects favor acylation at carbon. These divergent outcomes reflect marked differences in stability and reactivity of the available tautomers and indicate that, for dimedone-derived triketones, an alternative synthetic route is needed.

We then evaluated whether DMAP added to the reaction mixture could catalyze the *O*- to *C*-acyl rearrangement. We

found that after 4 h, a mixture of *O*-acylated (91%) and *C*-acylated (9%) products was generated (Table 1, entry 2); after 24 h, we observed a higher conversion to the desired triketone monomer (60%; Table 1, entry 3). Despite this improvement in yield, prospects for refining such a mixture of products would raise significant concerns for scale-up. Aside from DMAP, which appears to have limits in promoting *O*- to *C*-acyl rearrangements in reactions of dimedone with acid chlorides, we tested samarium(III) chloride (SmCl₃) and methanesulfonic acid (MSA), which have been shown previously to promote triketone formation, albeit with different substrates. The reaction of dimedone and sebacoyl chloride in the presence of SmCl₃ and triethylamine (NEt₃) in dichloromethane (CH₂Cl₂) produced exclusively the *O*-acylated product (Table 1, entry 4), while that with MSA produced only small amounts of the *O*-acylated product (15%), with most of the sebacoyl chloride undergoing rapid hydrolysis to sebacic acid (85%; Table 1, entry 5).

On the basis of these initial observations, we surmised that DMAP may be critical to achieving good conversion to the desired triketone monomer, yet its efficacy was diminished in reactions mixtures containing acidic byproducts. This led us to consider whether we should conduct the coupling of dimedone and the diacid chloride separate from the *O*- to *C*-acyl rearrangement. For the initial coupling step yielding the *O*-acyl product, our initial screen suggested that either SmCl₃ or an organic base could be considered. While full conversion of sebacoyl chloride to the *O*-acyl was observed by ¹H NMR at room temperature after 4 h, we found that the subsequent workup at scale involved a liquid–liquid extraction that was challenged by the persistence of samarium salts in both aqueous and organic phases. We then set out to optimize the yield and purity of the *O*-acyl product using a water-soluble organic base, where the workup would yield a more refined product. At a 10 g scale, we recovered the *O*-acylated product in 83% overall yield from dimedone and sebacoyl chloride in CH₂Cl₂ using pyridine as the base, requiring for the workup an aqueous extraction of the byproducts, evaporation of the reaction solvent, and recrystallization of the product from ethyl acetate.

Having optimized the production of the *O*-acylated intermediate, we next sought out to evaluate the efficacy of *O*- to *C*-acyl rearrangement using DMAP and potentially other

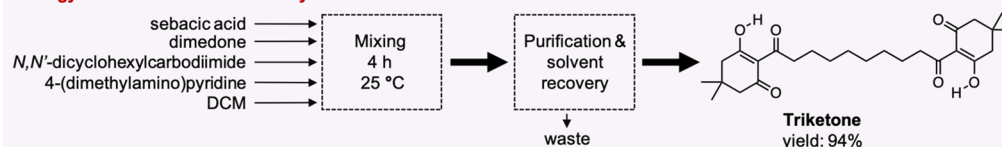
Table 2. C-Acylation of *O*-Acyl Intermediate to Triketone Monomer

entry	catalyst	solvent	[<i>O</i> -acyl] (M)	<i>T</i> (°C)	time (h)	<i>O</i> -acyl: cat.	isolated TK yield (%)
1	DMAP	toluene	0.6	100	4	1:2	90
2					24	1:0.1	94
3					24	1:0.05	97 ^a
4	AlCl ₃	DCM	0.11	20	24	4:1	17

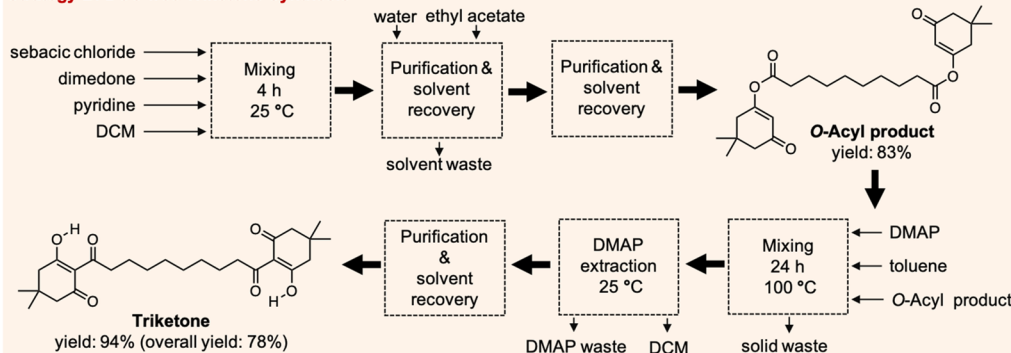
^aRecovered products exhibited heterogeneity in *O*- vs *C*-acylation, as noted in ¹H NMR.

1. MONOMER SYNTHESIS

Strategy A: DCC-based Triketone Synthesis



Strategy B: DCC-free Triketone Synthesis



2. POLYMER SYNTHESIS

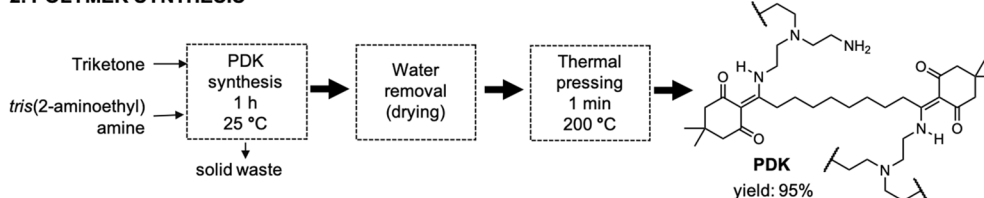


Figure 1. Simplified schematic for system boundary. (1) Monomer synthesis: strategy A refers to a DCC-based one-step triketone monomer synthesis previously published.^{13,15} Strategy B refers to systems analysis-informed DCC-free two-step synthesis developed for triketone production in this study. (2) Polymer synthesis is common for both triketone monomer synthesis strategies.

greener catalysts. With respect to the former, as hypothesized, we observed essentially quantitative conversion of the *O*-acyl product to the desired triketone in 4 h in toluene at an elevated temperature using a superstoichiometric quantity of DMAP (Table 2, entry 1). We next sought to determine whether DMAP could be implemented in catalytic amounts, given its quick action in promoting the rearrangement under these conditions (Table 2, entries 2–4). At a DMAP loading of 10 mol %, we isolated the desired triketone product cleanly in 94% yield after 24 h, with the longer reaction time accounting for the slower kinetics at a lower catalyst loading (Table 2, entry 3). Our further attempts to decrease the amount of DMAP yielded a mixture of products (*O*- and *C*-acyl products) under the same reaction conditions (Table 2, entry 4). For comparison, we also tested aluminum chloride (AlCl₃) as the

catalyst for *O*- to *C*-acyl rearrangement.³⁸ However, we found that AlCl₃ gave only low isolated yield (17%) of the triketone monomer (Table 2, entry 5). Trials at higher temperature or with AlCl₃ loadings were unsuccessful, and the workup was complicated by the need to aggregate the aluminum salts for more facile filtration, which we accomplished using Baekstrom's reagent. Nonetheless, we found that DMAP in catalytic amounts provided the most opportune circumstances for scale-up. In combining these two steps, we were able to produce the desired triketone monomer in 78% yield from dimedone and sebacoyl chloride, avoiding DCC and limiting the use of DMAP to only catalytic quantities. As these were the most problematic with regard to the sustainability of the primary production of PDK resins, we anticipated MSP, energy use, and life-cycle GHG emissions may be substantially lowered.

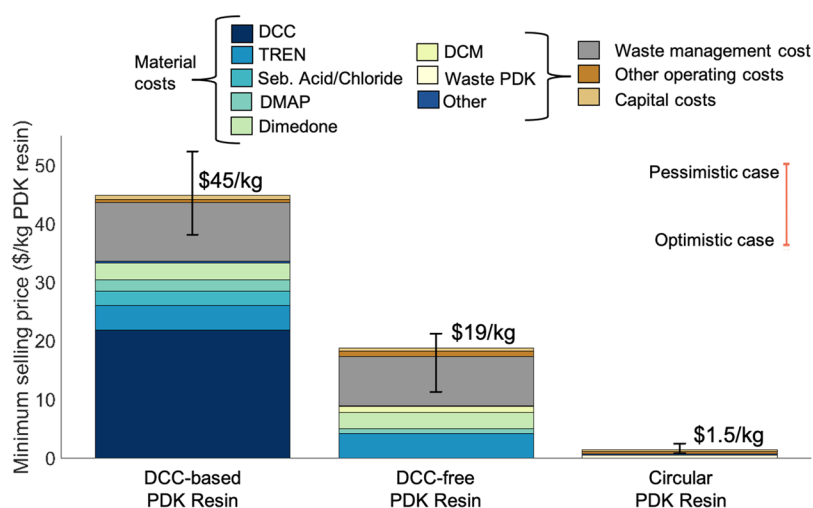


Figure 2. Minimum selling price contributions for PDK resin produced from (A) discovery chemistry (DCC-based PDK synthesis), (B) systems analysis informed chemistry (DCC-free PDK synthesis), and (C) chemical recycling (circular PDK resin). Breakdown is presented for the baseline case, and the error bar represents the sensitivity analysis in the results. DCC: *N,N'*-dicyclohexylcarbodiimide. DMAP: 4-(dimethylamino)pyridine. TREN: *tris*(2-aminoethyl)amine. DCM: dichloromethane.

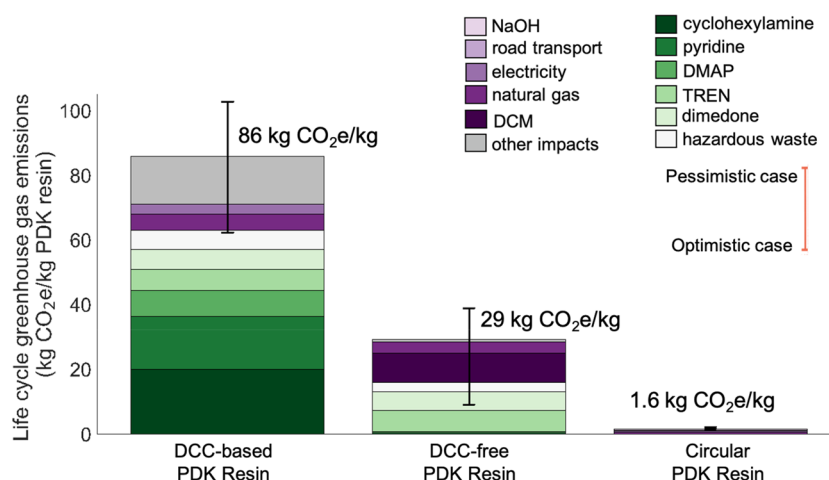


Figure 3. Life cycle GHG contributions for PDK resin produced from the discovery chemistry (DCC-based PDK resin), the current systems analysis-informed chemistry (DCC-free PDK resin), chemical recycling (circular PDK resin). The error bar represents the sensitivity analysis in the results.

Having established an alternative process for triketone synthesis, we depict the simplified system boundary diagram for two strategies for primary PDK production to compare them (Figure 1). The first panel describes the triketone monomer synthesis: Strategy A shows the DCC-based discovery chemistry,^{13,15} and strategy B demonstrates the DCC-free synthesis of triketone monomers developed here. The second panel depicts the polymer synthesis where the two essential building blocks for PDK production are triketone and *tris*(2-aminoethyl amine) (TREN). We assume triketone is synthesized on site and TREN is sourced externally. This methodology diagram aims to summarize the different steps of each process that has been simulated for the TEA and LCA studies.

Process Design and Technoeconomic Analysis. On the basis of the two strategies for synthesizing triketone monomers, we conducted a techno-economic analysis that reveals an MSP for the DCC-free primary PDK resin estimated at \$19 (\$11–21) per kg of PDK produced. The DCC based resin's MSP was estimated at \$45 (\$38–52), and circular PDK

resin's MSP was estimated to be \$1.5 (\$0.9–\$2.5) per kg of PDK produced (Figure 2). Thus, a 60% reduction of MSP was achieved with the alternative chemistry pathway when compared to the original discovery chemistry. The major driver of this price decrease is the elimination of DCC, which has a comparatively high bulk purchase price (\$17 per kg) and resulted in hazardous byproduct (*N,N'*-dicyclohexylurea, DCU) that requires expensive specialized disposal. The DCC-free chemistry resulted in a 73% reduction in total material costs and 16% reduction in waste management costs.

Regarding the details of DCC-free PDK synthesis, material costs account for 48% of the MSP, while waste management achieves 45% of this price. Among materials, TREN and dimedone contribute respectively 22% and 14% of the selling price. Both chemicals have the potential to be replaced by their biobased counterparts, which would assist in the transition toward reduced fossil carbon content and reduce downstream impacts of hazardous waste. Hazardous waste primarily arises from using a large quantity of solvents (dichloromethane, ethyl acetate) in the synthesis. While we assume 95% recycling for

all solvents in the system, a large quantity of dichloromethane is required to keep the reaction environment in dilution to maintain higher yields. Indeed, trials to lower both solvents in the *O*-acyl product synthesis and recrystallization steps led to lower yields.

Life Cycle Assessment. Similar to our observations in the techno-economic analysis, the DCC-free synthesis process reduced GHG emissions by 66% by decreasing upstream impacts of DCC production and downstream requirements of hazardous waste disposal. The life-cycle GHG emissions of DCC-free PDK synthesis sum to 29 kg of CO₂e per kg of PDK with sensitivity results ranging from 9–39 kg of CO₂e per kg of resin. This updated GHG footprint is 57 kg of CO₂e per kg of resin lower when compared to the DCC-based process (Figure 3). The largest contributors to GHG emissions in this updated process are the use of DCM (31%), followed by 23% from upstream production of TREN, and 20% from dimedone production. Natural gas contributes to 11% for GHG emissions and includes both natural gas required for on-site heat and electricity generation (direct impact) as well as used in upstream raw material productions (indirect impact). Electrification of industrial processes combined with a shift toward renewable fuels for heat-intensive processes could further reduce this GHG footprint. Solvent loss also contributes to the GHG emissions; we assume 95% recovery and reuse of solvents. The unrecovered 5% of all solvents is assumed to be lost to a mixed waste stream that must be incinerated, thus contributing to hazardous waste emissions (9% of total GHG emissions). This emissions footprint may ultimately be lower than presented here, depending on the mechanism of solvent loss and the fate of unrecovered solvents in the system.

The large variation in sensitivity analysis results primarily from GHG emissions characterization factors used for TREN (ranges from 4–44 kg CO₂e/kg) and dimedone (0.7–15 kg CO₂e/kg). Life-cycle GHG emissions values for these compounds are not readily available in the open literature. Scarcity of detailed data on production processes and associated emissions is a well-documented problem, particularly for specialty chemicals. Therefore, LCA characterization factors were estimated based on the compound's structural similarity to other compounds with known data using tools developed by Song et al.³⁹ and Wernet et al.⁴⁰ The ranges presented for these chemicals in the sensitivity analysis reflect the upper and lower bounds based on the emissions footprint for synthesis of the most structurally similar compounds. Another alternative approach would be to use patents to construct process models for manufacturing these chemicals, as Neupane et al.²¹ did to reconstruct likely synthesis routes for ionic liquids that are not well documented in the open literature. Such an approach also has drawbacks; patents only provide a general map/guideline of synthesis, and manufacturing details are proprietary. However, we did employ this process simulation strategy in the case of sebacoyl chloride, with additional input and confirmation from industry experts. Despite the considerable uncertainty, our results provide a definitive indication that life-cycle GHG emissions are reduced in the DCC-free PDK synthesis route. Furthermore, because of the commonalities in chemical inputs across both synthesis routes, the relative differences in emissions footprints will remain largely unchanged.

PDK Resin Use in Automotive Industry. To further compare the implementation of PDK circularity with an existing market, we have targeted PU products used in the

automotive sector as case studies. We selected automotive end-uses because of the high likelihood of material recovery (for example, 99% of lead-acid batteries are recovered at their end-of-life), which is crucial for PDK, given the wide gap between the cost of virgin material and recycled PDK. We also selected PU for replacement because of the limited options for PU recycling and the potential for PDK to achieve comparable properties for rigid and flexible PU applications. PU has limited competing options for recycling. Mechanical options, such as rebinding or compression molding, result in inferior properties, and the separations and purification costs remain high for chemical processes such as glycolysis.⁴¹ Polymers in cars are not generally recycled; after metals are recovered, remaining materials in cars are shredded to produce automotive “fluff” for disposal.⁴² On the basis of U.S. practices, we assume this automotive shredder residue is landfilled in a business-as-usual scenario. Although this fluff would be very difficult to handle in a mechanical recycling process because of the levels of contamination from mixed plastics and metals, prior experimental work has demonstrated the ability to chemically recycle PDK resins when metals, glass, adhesives, and other polyolefins are present, suggesting that PDKs could successfully be recovered from these heterogeneous ASR mixtures.¹⁴

Three different scenarios were envisaged over a 60-year timespan: either (A) 99% or (B) 44% of the virgin PDK has been recycled and (C) 99% of the circular PDK has been recycled. In scenarios A and B, virgin PDK must first be introduced into the market and later recovered to begin increasing the fraction of recycled PDK in circulation. In scenario C, the system operates in a long-term steady state with only minimal virgin PDK required to compensate for recovery and recycling losses. Virgin PDK production results in higher GHG emissions (29 kg CO₂e/kg resin) compared to PU production (3 kg CO₂e/kg resin), resulting in an initial spike during the first few years of using virgin PDK as makeup (before significant waste can be recovered back; Figure 4A). These emissions accumulate over the years. Despite 99% recycling, at the end of 60 years, the use of PDK results in twice as much emissions (0.3 billion metric tons CO₂e) as PU (0.1 billion metric ton CO₂e). With 44% recycling of PDK (with virgin makeup PDK added), the emissions amount to 0.7 billion metric tons of CO₂e. However, this disparity is to be expected; our analysis explores an early stage novel material (PDK) with PU, which was commercialized over 80 years ago. If we assume the system is in a steady state, with circular PDK production as a mature technology, and that sufficient waste PDK is available to meet ongoing market demand, then cumulative GHG emissions with aggressive 99% recycling would amount to 0.06 billion metric tons of CO₂e, half that of PU. One of the key takeaways from Figure 4A is the need to increase recovery and recycling rates, which will be essential to enabling a wide range of novel recyclable materials and recycling processes.

Separate from GHG emissions, plastic waste accumulation in landfills is an important undesired effect of the extensive use of short lifetime plastics. To track waste accumulation, we have created a model to compare PDK and PU products from transportation scrap over the next 60 years (Figure 4B). On the basis of the two recycling scenarios from virgin PDK (44% and 99%), we assume that respectively 56% and 1% waste PDK ends up in landfill, and the rest is recycled back into the system. The use of both PU and PDK follows the log-normal modeling of end of life for vehicles. As such, resin

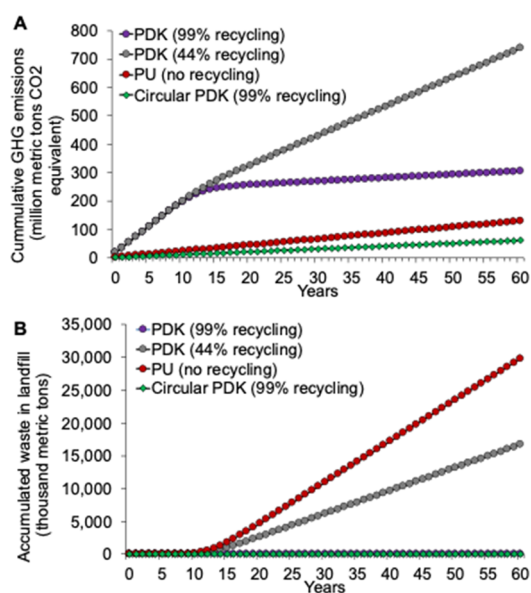


Figure 4. Evolution over 60 years of (A) cumulative life cycle GHG emissions and (B) waste accumulated in landfill with different PDK recycling scenarios and use of polyurethane (PU). PDK results refer to mixed PDK with X% of PDK coming from recycled feedstock and the rest comprised of virgin material produced through DCC-free synthesis.

manufactured in year 1 would only be fully recovered after ~20 years. We do not consider supply chain losses, mismanaged waste, and waste that leaks into the environment. For PU used in the automotive industry, we expect 30 million metric tons of waste would be accumulated in the landfills, and in comparison, 17 million metric tons of PDK waste would be accumulated in the landfill with a 44% recycling scenario. With an aggressive recycling target of 99%, we would accumulate only 0.03 million metric tons of waste PDK, diverting over 1000 times more waste from landfills. In future analyses, considering the cost and emissions trade-offs (or cobenefits) per tonne of waste diversion from landfills, incinerators, or other fates can be a useful framework for evaluating novel polymers and recycling strategies.

CONCLUSION

Lowering the barrier to market entry and ensuring sustainable production of highly recyclable plastics near term are critical to realizing their promise to the economy and the environment. For circular PDK resins, our systems analysis identified triketone monomer production as a prime target for further development to inform future best manufacturing practices. In this work, we demonstrate significant progress in improving the sustainability of triketone monomer production using a two-step process that avoids reagents producing high volumes of hazardous waste and implements a catalyst in a key step to ensure that the triketone monomer is isolated in high yield and high purity. In the second step of the process, which involves an *O*- to *C*-acyl transfer, we found reaction conditions that reduce the catalyst loading by an order of magnitude. With this two-step synthetic route, MSP and life-cycle GHG emissions for PDK resin production were reduced by 57% and 66%, respectively. Notably, primary production of PDK resins remains 13 times more expensive than circular PDK resins, which serves as a clear incentive to recover the maximum amount of waste PDK possible and to explore further supply

chain opportunities. For example, dimedone and TREN are now major contributors to MSP and GHG emissions. We anticipate that biobased and bioengineered 1,3-ketones and amine monomers will open an avenue for reducing GHG emissions further, while also addressing the resilience of the PDK supply chain in the long term.

We also explore the potential for PDK resins to address a specific market segment suffering from the implications of plastic waste on the sustainability of products serving that market. Specifically, we consider the impact of replacing nonrecyclable PU resin used in the automotive industry with circular PDK resin over the next 60 years. We found that even with the current improvements to PDK production, GHG emissions may still be higher than PU, although GHG emissions savings can be substantial in a steady-state case where little or no virgin PDK is required and the industry has reached near-circularity. Targeted collection and sorting strategies need to be properly executed once PDK reaches commercial scale. Such strategies may be more straightforward to implement for vehicles, particularly if original equipment manufacturers opt to play a more active role in dismantling and recycling components of their vehicles at their end-of-life. For other applications, such as single use plastics, optimistic recovery rates nearing 99% are simply out of reach given today's infrastructure. Our analysis, therefore, defines several "AND problems" intrinsic to circular plastics that must be solved to raise the benefits and lower the burdens associated with plastics in an ideal circular economy. Our work also highlights the importance of bringing life-cycle assessment and techno-economic analysis to the development of circular polymers, processes, products, and business models at the earliest stage possible to understand and overcome barriers to entering the market. Our strategy for quantifying the costs and benefits of PDK circularity may serve as a guidepost for other circular polymers also seeking to improve global health through reductions in GHG emissions and plastic waste.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.1c07851>.

Synthesis and characterization details, additional life-cycle assessment and cost modeling results, as well as underlying assumptions and parameters (PDF)

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Notes

The authors declare the following competing financial interest(s): B.A.H. is an inventor on U.S. provisional patent application 62/587,148 submitted by Lawrence Berkeley National Laboratory that covers poly(diketoenamine)s, as well as aspects of their use and recovery. J.D.K. has a financial interest in Amyris, Lygos, Demetrix, Napigen, Maple Bio, Apertor Labs, Berkeley Yeast, Ansa Biotechnologies, and Zero Acre Farms.

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