Polydiketoenamines (PDK): The Promising Newcomer in Sustainable Plastic Innovation and Circular Economy

-a Mini Review-

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Abstract

Polydiketoenamines (PDK) is an emerging plastic material with an attractive feature that can be fully recycled to its monomers for reuse, thus paving the way for a responsible plastic manufacturing and circular economy. This mini review will address the synthesis, properties, and the recyclability of PDK.

1. Introduction

Plastics have become pervasive in virtually every facet of modern society, making them the most widely used synthetic material (Sánchez et al, 2011; Worm et al, 2017). Its inherent properties, such as durability, plasticity, transparency, and inertness, contribute to its persistent nature in the environment, resulting in the pressing issue of plastic accumulation. In fact, plastics account for 20% of total waste by volume in landfills, rendering landfill an unsustainable option due to plastic's extended degradation time (Sánchez et al, 2011). Efficient recycling of plastic waste has been identified as the next major challenge for the plastic recycling sector and needs the development of new processes (Hopewell et al, 2009). Current recycling practices use mechanical grinding, melt filtration, extrusion, and pelletization to produce resins for secondary manufacturing. However, these processes degrade the polymer properties through chain scission, resulting in a decrease in molecular weight which affect the viscoelastic properties of polymer melts. Without a way to upgrade recycled materials to make them more valuable (e.g., through a solvent-assisted process to produce food-grade resin by removing additives, impurities, and oligomers), the economic feasibility of this current recycling practices may not be profitable enough to encourage large-scale recycling efforts. Chemically recycling plastic waste to reusable monomers is regarded as the key to unlocking circularity, provided the process can be conducted efficiently in a closed loop. Although this has been difficult to achieve in current practice, there is a newly discovered materials called polydiketoenamines (PDK) which can pose as circular polymers for a new plastics economy (Helms, 2022). PDK resins are produced from commercially available amine monomers and novel triketones, which are synthesized from 1,3-diketones and dicarboxylic acid (Demarteau et al, 2022). PDK resins exhibit characteristics of both thermoplastics and thermosets because of their dynamic bonding, which is well-documented and unique to dynamic covalent polymer networks (Scheutz et al, 2019; Jin et al, 2019; Yue et al, 2020). PDK resins can recover virgin-quality monomers at comparatively high yields (90−99%, depending on formulation) relative to other chemical recycling strategies (Demarteau et al, 2022). The properties of PDK resins that can be manufactured, used, recycled, and re-used without losing value, indicates promising possibilities for creating sustainable polymers with minimal environmental impact (Christensen et al, 2019).

2. Polydiketoenamines (PDK) Resin

2.1. Synthesis of PDK

Generally, PDK resins can be synthesized from polytopic triketone and amine monomers (Figure 1) that condense spontaneously, producing water as the sole by-product.

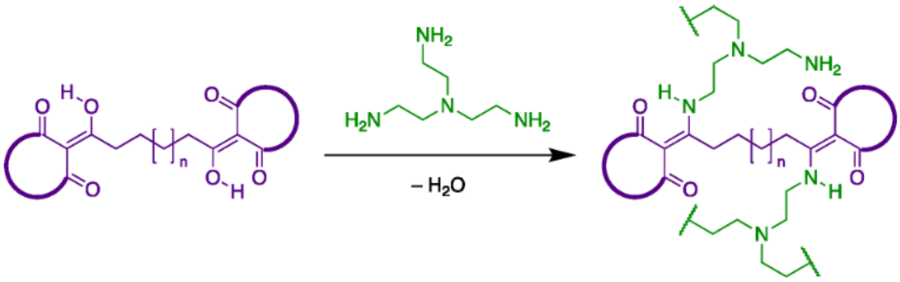

Figure 1. Synthesis of PDK resins
[Source: Helms, 2022]

The triketone monomers are synthesized from polytopic 1,3-diketones and carboxylic acids (or preactivated esters) via chemical condensation. Depending on the exact chemistry of the 1,3-diketone, C-acylation may occur at carbon (thermodynamic product) or at oxygen (kinetic product). Exclusive C-acylation affords the desired triketone monomer, thus regiospecificity is an important aspect of monomer design and synthesis (Helms, 2022).

The amine monomers used in the synthesis are varied based on their molecular weight, number, and spacing of appended amines, conformational degrees of freedom, crystallinity, and other characteristics that can be used to impart specific properties to PDK resins. The broad palette of polytopic triketone and amine monomers available permits the creation of thermoplastics, elastomers, and thermosets with unique architectures as well as useful and tunable properties for a range of applications (Helms, 2022).

2.2. Formulation and Properties of PDK

Extensive research has been conducted on the properties and formulation of PDK materials through various chemical techniques, particularly with the resins cross-linked with tris-(2-amino-ethyl)-amine (TREN). These investigations have explored differences in cross-linking density and conformational degrees of freedom, enabling PDK materials to be designed with specific properties such as strength, flexibility, and thermal stability, making them suitable for various applications. One way to create PDK materials with unique properties is by changing the length of the carbon spacer between triketone moieties in the monomer, resulting in a PDK material that blurs the line between thermoplastics and thermosets. Moreover, the properties of PDK can also be modulated by combining certain diamine monomers with TREN in prescribed ratios, which affects their network density, and thus their thermal, mechanical, and rheological properties. In addition, PDK incorporated with polyetheramines have also been investigated, resulting in the production of plastic that is harder, tougher, and easier to reprocess from scrap. By lowering the cross-linking density, PDK materials can become more product-ready, manufacturable, and recyclable. Furthermore, PDK elastomers and thermosets can be thermally processed during manufacturing and reprocessed during scrap recovery with resilience due to the dynamic covalent character of the diketoenamine bond (Helms, 2022).

Comparing to other plastics materials, PDK resins have similar properties to polyurethanes (PU) and nylon. PU can be 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. In recycling process for nylon, extensive cleaning and removal of unwanted contaminant is required which is very costly. 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 PU rubbers (0.6−44.1 MPa) (Demarteau et al, 2022). With these similarity, PDK resins offers a more sustainable recycling alternative with more advantaged properties.

2.3. Scrap Recovery with PDK Resins

Scrap recovery is a process of collecting and recycling materials that is considered as waste and can be achieved through a variety of methods such as mechanical separation, chemical processing, and thermal treatments. Scrap recovery is desirable for maximizing recycling efficiency. Polymers that feature dynamic bonds, such as vitrimers, can enable scrap recovery (Helms, 2022). Vitrimers are a living polymer networks that reconfigure via dynamic associative bond-exchange reactions, laying the foundations for both self-healing plastics and post-industrial plastics recycling (He et al, 2020). PDK resins is classified as a vitrimers due to their unique chemistry to uncouple (Christensen et al, 2019) and design for infinite recyclability (Demarteau et al, 2022). PDK could be designed with dynamic covalent bond for creating vitrimers with a low energy requirement for scrap recovery (Helms, 2022). The low activation barrier for aromatic amine monomers enables their use in PDK formulations that are harder and tougher, whereas previously, these performance-enhancing monomers were difficult to incorporate and use in imine and vinylogous urethane vitrimers for efficient scrap recovery (Helms, 2022).

2.4. Chemical Recycling of PDK Resins

Chemical recycling of PDK resins can happen at ambient temperature in strong acid, yielding insoluble triketone monomers and soluble amine monomers (Helms, 2022). Depolymerization is faster when using higher concentrations of acid (typically 1−5 M is used) or when conducting the acidolysis process at elevated temperature. Depolymerization is generally complete within 12−24 h (Figure 2a). In 5M H_2SO_4, complete depolymerization occurs in less than 12h, and pure triketone and amine monomers are recovered in >90% isolated yields. Corresponding data showed that the amount of PDK remaining after 24 hours is decreasing with the increase of the concentration of H_2SO_4 used (Figure 2b) (Christensen et al, 2019).

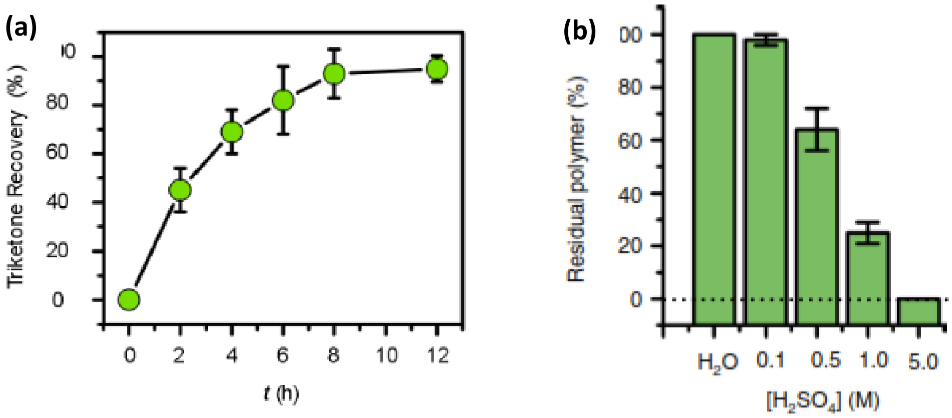

Figure 2a. Depolymerization of TREN-based PDK
Figure 2b. Amount of PDK remains as a function of acid concentration
[Source: Christensen et al, 2019]

From these data, we can investigate the relationship of H_2SO_4 concentration and time on the depolymerization of PDK. If we compare the concentration of H_2SO_4 used with the depolymerization time, we can see that as the concentration of H_2SO_4 increased, the depolymerization time decreased, indicating a more efficient and rapid breakdown of PDK into its monomers (Figure 3).

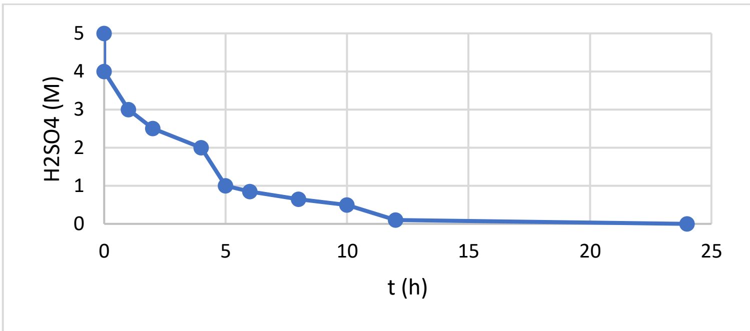

Figure 3. PDK depolymerization as a function of acid concentration vs time
[Reprocessed data from Christensen et al, 2019]

Insoluble triketone monomers are recovered by filtration and refined by resolubilization in aqueous base and then reprecipitation upon addition of strong acid (Helms, 2022). The amine monomer (e.g., TREN), is recovered using a regenerative resin-based process (Christensen et al, 2019). The depolymerization of PDK under acidic conditions enable additives to be separated from the monomers, ensuring monomer recovery in high yield (typically >90%) and high purity (typically >99%) (Helms, 2022).

One example for separation of additives from the monomer is pigments. PDK particulates loaded with different pigments (e.g., carbon black) are depolymerized in strong acid, which produces a mixture with multiple phases. The solid from this mixture contains the triketone monomer and can be isolated by filtration. Once isolated, the triketone is made soluble by adding a base. After filtering the remaining solids, the filtrate containing the triketone is acidified to precipitate it (Figure 4a). Another example of separation is plasticizers.

Triphenylphosphate (TPP), a widely used plasticizer and flame retardant, were able to be retrieved as solids after depolymerization of PDK resin compounded with TPP was conducted. When the composite was deconstructed in strong acid, the fiber was retrieved, and the mixture containing insoluble triketone monomer and TPP solids were filtered to isolate the amine monomers. Base was then added to solubilize the triketone monomer. The mixture was then filtered to isolate the TPP. Acidification of the mixture were then conducted to precipitate the triketone monomer and filtered the mixture, isolating the triketone monomer for reuse (Figure 4b) (Christensen et al, 2019).

Under the same conditions, depolymerization is not observed for common plastics, allowing PDK to be easily separated from mixed plastic waste streams (Figure 5) (Christensen et al, 2019).

Figure 4a. Depolymerization of PDK particulates loaded with different pigments in strong acid
Figure 4b. Deconstruction of a fiber-reinforced PDK composite loaded with flame retardant
[Source: Christensen et al, 2019]

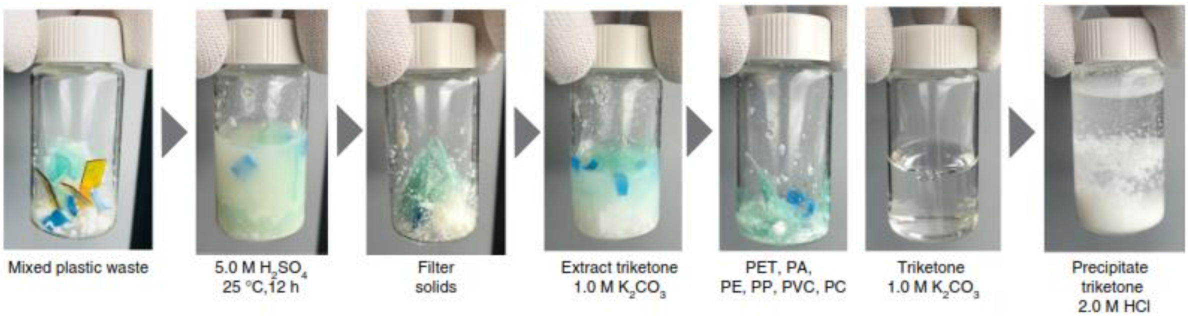

Figure 5. Recovery of triketone monomer from mixed plastic waste containing PDK, PET, PA, PE, PP, PVC, PC
[Source: Christensen et al, 2019]

2.5. Closed-loop Circular Economy with PDK Resins

When PDK resins reach the end of their life, products made from PDK resins can be chemically recycled to their original monomers through ambient temperature acidolysis. This process is highly effective as the contrasting properties of triketone and amine monomers allows them to be isolated from one another with low cycle-to-cycle losses, suggesting infinite recyclability. The monomers obtained through this process are of high purity, making them immediately reusable in circular PDK manufacturing. Moreover, other components such as pigments, additives, flame retardants, fillers, and fibers can also be recovered in pristine condition. This recovery of all components offers a sustainable approach to plastic production by preventing waste and reducing the need for new materials. The ability to reuse all components and the potential for infinite recyclability make PDK resins a valuable material for circular manufacturing (Helms, 2022).

Furthermore, the recovery of triketone and amine monomers enables their immediate re-use for synthesizing new polymers of the same or different formulation, maximizing the inherent value of waste material. The recovered monomers can also be re-formulated into PDK resins with the same or differentiated properties. This transition from recycling to upcycling creates a higher value product from waste materials, which is an important step towards a more sustainable and circular economy for plastics (Christensen et al, 2019).

3. Conclusions

PDK resins emerge as a promising solution for creating a sustainable and circular plastic economy (Christensen et al, 2019). As the issue of plastic waste has become a global concern, PDK offer transformative opportunities to close the loop in plastics production, use, loss-less recovery, and reuse. To fully exploit the potentials of this material, it is necessary to do more in-depth research on how combinations of specific monomers can affect the properties of PDK. Additionally, understanding the effect of different triketone or amine monomer combinations on recycling efficiency is crucial, particularly regarding any necessary chemical separations during deconstruction to recovered refine monomer mixtures (Helms, 2022). With continued efforts to understand and optimize PDKs, these materials could help pave the way towards a more responsible and sustainable future for plastic manufacturing.

References

Christensen, P. R., Scheuermann, A. M., Loeffler, K. E., & Helms, B. A. (2019). *Closed-loop recycling of plastics enabled by dynamic covalent diketoenamine bonds*. Nature chemistry, 11(5), 442-448.

Demarteau, J., Vora, N., Keasling, J. D., Helms, B. A., & Scown, C. D. (2022). *Lower-cost, lower-carbon production of circular polydiketoenamine plastics*. ACS Sustainable Chemistry & Engineering, 10(8), 2740-2749.

He, C., Christensen, P. R., Seguin, T. J., Dailing, E. A., Wood, B. M., Walde, R. K., ... & Helms, B. A. (2020). *Conformational entropy as a means to control the behavior of poly (diketoenamine) vitrimers in and out of equilibrium*. Angewandte Chemie International Edition, 59(2), 735-739.

Helms, B. A. (2022). *Polydiketoenamines for a Circular Plastics Economy*. Accounts of Chemical Research, 55(19), 2753-2765.

Hopewell, J., Dvorak, R., & Kosior, E. (2009). *Plastics recycling: challenges and opportunities*. Philosophical Transactions of the Royal Society B: Biological Sciences, 364(1526), 2115-2126.

Jin, Y., Lei, Z., Taynton, P., Huang, S., & Zhang, W. (2019). *Malleable and recyclable thermosets: The next generation of plastics*. Matter, 1(6), 1456-1493.

Sánchez, A. C., & Collinson, S. R. (2011). *The selective recycling of mixed plastic waste of polylactic acid and polyethylene terephthalate by control of process conditions*. European Polymer Journal, 47(10), 1970-1976.

Scheutz, G. M., Lessard, J. J., Sims, M. B., & Sumerlin, B. S. (2019). *Adaptable crosslinks in polymeric materials: resolving the intersection of thermoplastics and thermosets*. Journal of the American Chemical Society, 141(41), 16181-16196.

Worm, B., Lotze, H. K., Jubinville, I., Wilcox, C., & Jambeck, J. (2017). *Plastic as a persistent marine pollutant*. Annual Review of Environment and Resources, 42, 1-26.

Yue, L., Guo, H., Kennedy, A., Patel, A., Gong, X., Ju, T., ... & Manas-Zloczower, I. (2020). *Vitrimerization: converting thermoset polymers into vitrimers*. ACS Macro Letters, 9(6), 836-842.