

Closed-loop recycling of plastics enabled by dynamic covalent diketoenamine bonds

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Recycled plastics are low-value commodities due to residual impurities and the degradation of polymer properties with each cycle of re-use. Plastics that undergo reversible polymerization allow high-value monomers to be recovered and re-manufactured into pristine materials, which should incentivize recycling in closed-loop life cycles. However, monomer recovery is often costly, incompatible with complex mixtures and energy-intensive. Here, we show that next-generation plastics—polymerized using dynamic covalent diketoenamine bonds—allow the recovery of monomers from common additives, even in mixed waste streams. Poly(diketoenamine)s ‘click’ together from a wide variety of triketones and aromatic or aliphatic amines, yielding only water as a by-product. Recovered monomers can be re-manufactured into the same polymer formulation, without loss of performance, as well as other polymer formulations with differentiated properties. The ease with which poly(diketoenamine)s can be manufactured, used, recycled and re-used—without losing value—points to new directions in designing sustainable polymers with minimal environmental impact.

Closed-loop polymer life cycles are critical to sustainability efforts worldwide^{1–7}. Their integration into the global materials' ecosystem hinges on maintaining high value in recovered materials at the end of a product's life. Value is lost when processing is costly, energy-intensive or alters the physical properties and appearance of recovered materials⁸. To reduce the cost and energy intensity of depolymerizing plastics, lowering the energetic barrier to bond cleavage is critical. Advances in catalysis⁹ and dynamic covalent chemistry¹⁰ have emerged as potential solutions^{11–35}. In particular, dynamic covalent polymers known as vitrimers have been recently proposed as sustainable replacements for non-recyclable thermoset materials^{27–35}. Vitrimers undergo associative bond exchange reactions in the solid state, allowing crosslinked materials to be thermally processed and recycled like thermoplastics while maintaining high crosslink density. In certain cases, vitrimers have been shown to depolymerize, yielding soluble oligomers or small molecules (Supplementary Fig. 1)^{28,30–32,34,35}. However, like other plastics, it remains a challenge to depolymerize vitrimers at low temperatures, in short reaction times, with high tolerance to additives, and from mixed plastic waste streams. Furthermore, depolymerization efforts have not emphasized a return to the original monomers, which limits re-formulation opportunities by requiring further manipulation before re-entering the supply chain.

Here we show that dynamic network polymers synthesized using diketoenamine bonds address these challenges by leveraging their unique chemistry to uncouple the otherwise conflicting demands for formulation, manufacturing, performance, recycling, re-manufacturing and re-use. Poly(diketoenamine)s, or PDKs, are prepared via ‘click’³⁶ polycondensation reactions between β -triketones and aromatic or aliphatic amines (Fig. 1). Notably, β -triketone monomers are accessed in a single step from widely available polytopic carboxylic acids and 1,3-diones³⁷. In contrast to other vitrimer platforms (Supplementary Fig. 1), PDKs hydrolyze in strong aqueous acid (0.5–5.0 M H_2SO_4) at ambient temperature to yield pure, immediately reusable triketones (Supplementary Fig. 2); amine monomers are then

recovered using a regenerative resin-based process, closing the loop (Fig. 2a and Supplementary Fig. 3). In 5.0 M H_2SO_4 , complete depolymerization occurs in less than 12 h, and pure triketone and amine monomers are recovered in >90% isolated yields (Fig. 2b–d); 5.0 M HCl was similarly effective in PDK depolymerization. Under the same conditions, depolymerization is not observed for common plastics in use today, allowing PDKs to be easily separated from mixed plastic waste streams (Fig. 2e). PDK depolymerization also tolerates a wide spectrum of additives, including dyes, pigments, inorganic fillers, fibre reinforcing fabrics and flame retardants, even when these additives comprise high weight fractions in the polymer composite. Recovered monomers can be re-manufactured without loss of performance, or re-formulated with differentiated properties. The ease with which PDKs can be manufactured, used, recycled and re-used—without losing

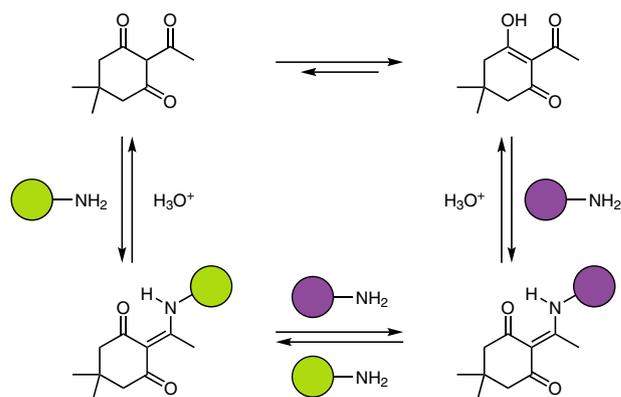


Fig. 1 | Reversible, dynamic covalent diketoenamine bonds. Diketoenamine bonds form spontaneously from triketones and both aromatic and aliphatic amines. Under strongly acidic conditions in water, the diketoenamine bond hydrolyses to the triketone and an ammonium salt.

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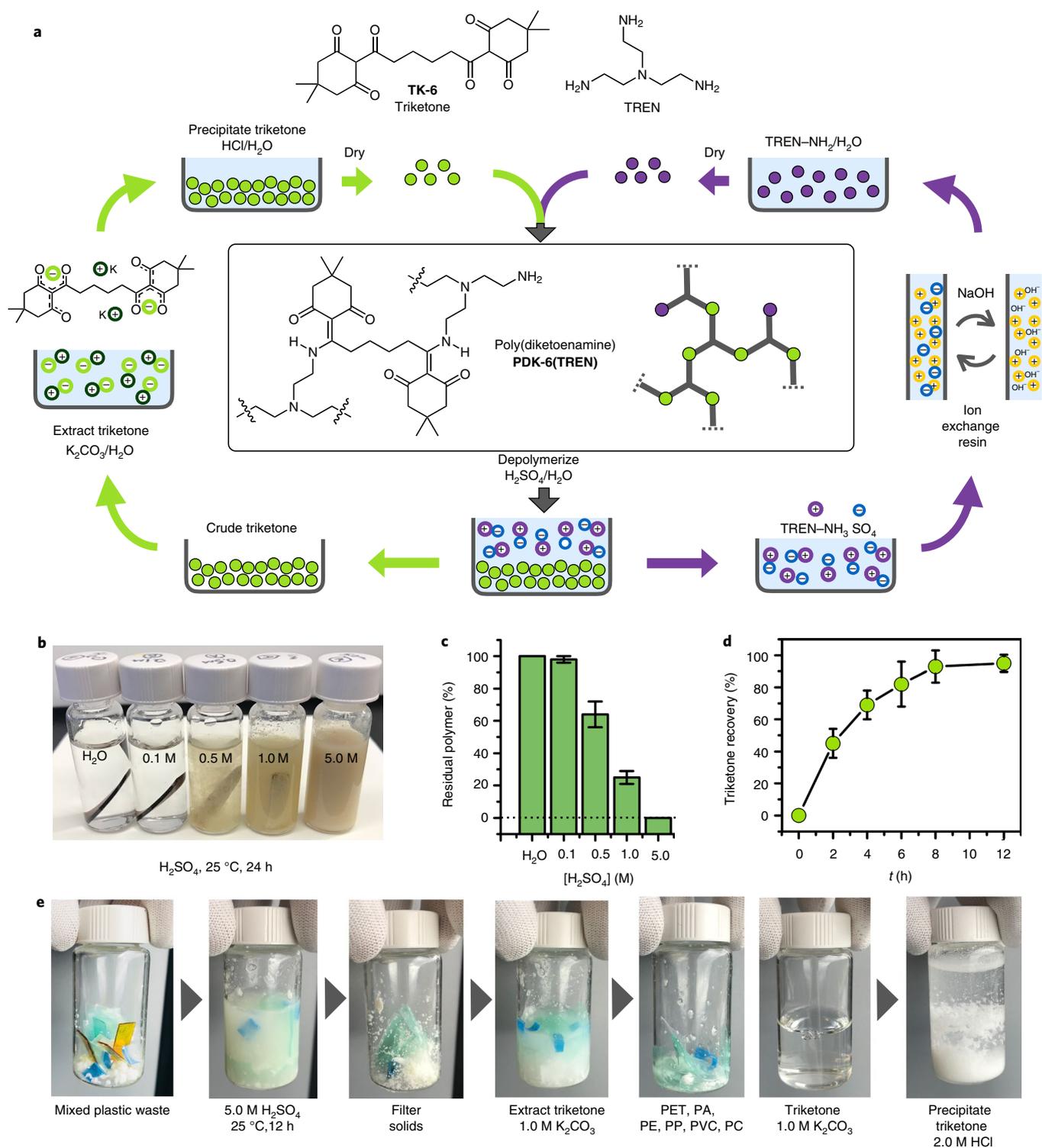


Fig. 2 | Closed-loop recycling from dynamic covalent PDKs. **a**, Network PDKs (for example, **PDK-6(TREN)**) are synthesized from polyamines (for example, tris(2-aminoethyl)amine, TREN) and ditopic triketones (for example, **TK-6**), and are hydrolysed in strong acid. Both triketone and TREN monomers can be recovered and re-used in a closed-loop fashion using regenerative chemical processes. **b**, Photograph showing the depolymerization of **PDK-6(TREN)** in H_2SO_4 from 0 to 5.0 M. **c**, Corresponding data showing the amount of PDK remaining after 24 hours at room temperature as a function of acid concentration. **d**, Triketone monomer recovery over time during **PDK-6(TREN)** depolymerization in 5.0 M H_2SO_4 . **e**, Photographs showing orthogonal depolymerization of PDKs and triketone monomer recovery from mixed plastic waste containing poly(ethylene terephthalate) (PET), nylon-6,6 (PA), polyethylene (PE), poly(vinyl chloride) (PVC) and polycarbonate (PC). Data in **b** and **c** are the average of two trials; error bars indicate s.d.

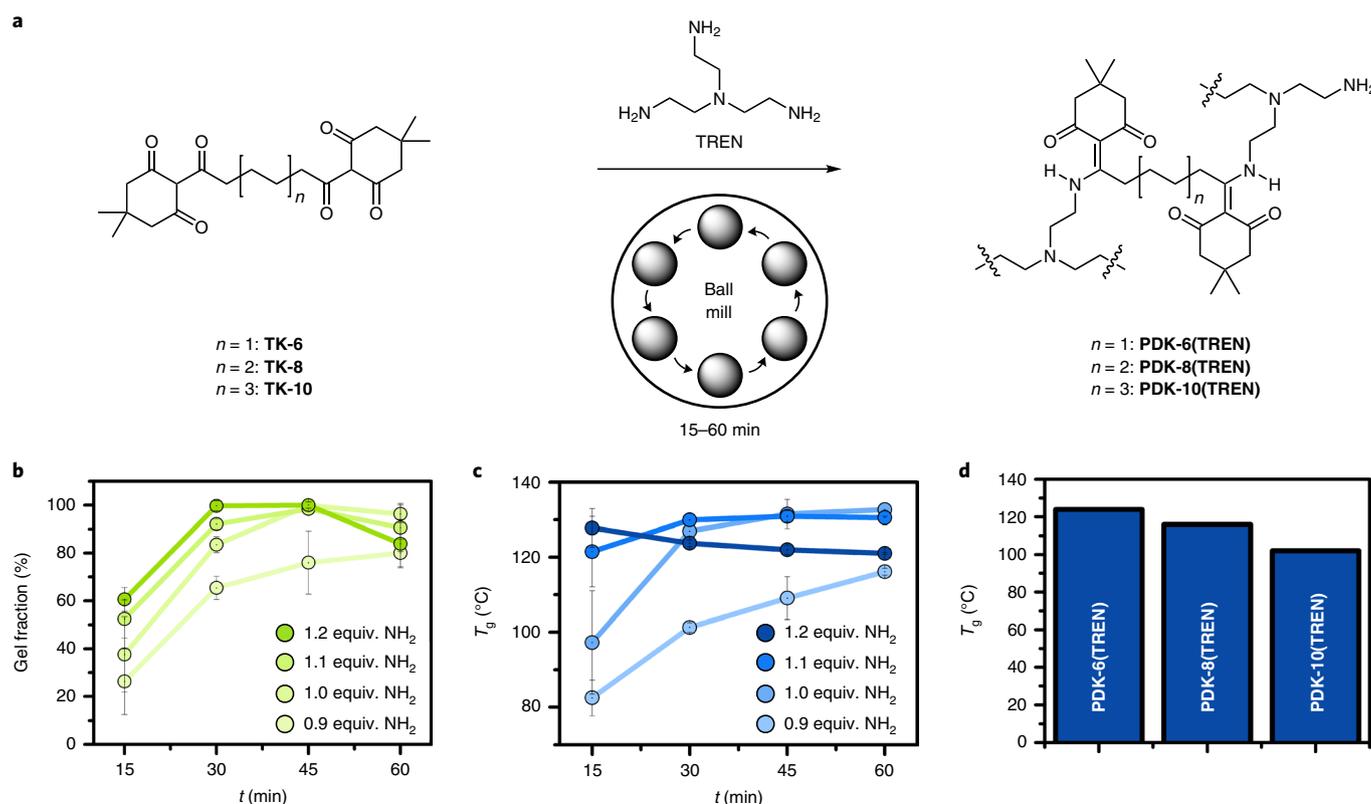


Fig. 3 | Synthesis of network poly(ketoenamine)s by ball-milling. **a**, Dynamic covalent PDKs are synthesized by ball-milling TK-6–10 with TREN, yielding network polymers PDK-6–10(TREN). **b,c**, A well-controlled PDK network density is evidenced by repeatable trajectories for the gel fraction (**b**) and T_g (**c**), each as a function of ball-milling time and the mol% (equiv.) of amine functionality relative to triketone functionality in the formulation. Data are shown for PDK-6(TREN). **d**, The observed T_g of different PDK networks decreases with increasing triketone spacer length. Data in **b, c** are the average of three trials; error bars are the standard deviation.

value—suggests exciting new paths for next-generation plastics with minimal environmental impact.

Results

Polymer synthesis. The PDK platform encompasses a broad range of polymer formulations for accessing diversity-oriented structure–property space. To begin to explore PDK structure–property space, we prepared three triketone dimers from adipic acid (TK-6), suberic acid (TK-8) and sebacic acid (TK-10) precursors, respectively (Fig. 3). Owing to the spontaneous reaction between amines and triketones, PDK networks are easily synthesized by mechanically grinding triketone monomers with tris(2-aminoethylamine) (TREN) or with mixtures of TREN and various diamines using a ball mill, without requiring organic solvents. In addition to being a scalable process, we hypothesized that the extent of reaction between amines and triketones could be controlled by adjusting the ball-milling time. To demonstrate this, TK-6 was ball-milled in the presence of TREN, without solvent, yielding fine powders of network polymer PDK-6(TREN) (Supplementary Fig. 4). The glass transition temperature T_g and insoluble (gel) fraction of PDK-6(TREN) were measured as a function of both the duration of ball-milling and equivalents (equiv.) of amine relative to triketone functional groups (Fig. 3e,f). PDK-6(TREN) network materials showed high T_g (>120 $^{\circ}\text{C}$) and gel fractions of >95% in less than 1 h of mechanical processing. The extent of the reaction was further analysed by solid-state NMR spectroscopy, showing no detectable TK-6 starting material after only 45 min of ball-milling for formulations with ≥ 1 equiv. amine (Supplementary Figs. 5–9). The reproducible trajectories of both T_g and gel fraction as a function of formulation and process-

ing time are an advantage over batch processes where these cannot be controlled, indicating that ball-milling is a powerful new tool for controlling network density in dynamic soft matter.

Polymer compounding, de-colouration and recovery of virgin-quality monomer. We found ball-milling to be effective in blending various stabilizers, plasticizers, dyes, pigments and flame retardants into the polymers to meet aesthetic, performance and regulatory requirements without complicating recycling. To demonstrate this, network polymer PDK-6(TREN) was recycled as a mixture of coloured plastics containing organic and inorganic colourants (Fig. 4). Red, blue, yellow and black samples of PDK-6(TREN) were mixed together and depolymerized in 5.0 M H_2SO_4 to yield a precipitate containing TK-6 monomer along with carbon nanofibres, TiO_2 and red, blue and yellow dye molecules. From complex mixtures, triketone monomers are easily separated from additives, and other polymers, by extracting into aqueous base, filtering off insoluble components and subsequently precipitating triketones upon re-acidification ($\text{pH} < 3$) (Fig. 4c,d).

Closed-loop recycling of flame-retardant fibre-reinforced composites. Depolymerization strategies, such as ours, are attractive for recycling fibre-reinforced composite materials^{31,32}, and PDKs may be particularly well suited for these applications. To demonstrate the ease of depolymerization and separation of all components in such composites, woven fibreglass was impregnated with a PDK-6(TREN) resin containing 25% (wt/wt) triphenylphosphate (TPP) as a flame retardant (Supplementary Fig. 10). The fibre-reinforced composite was subjected to the described aqueous processing

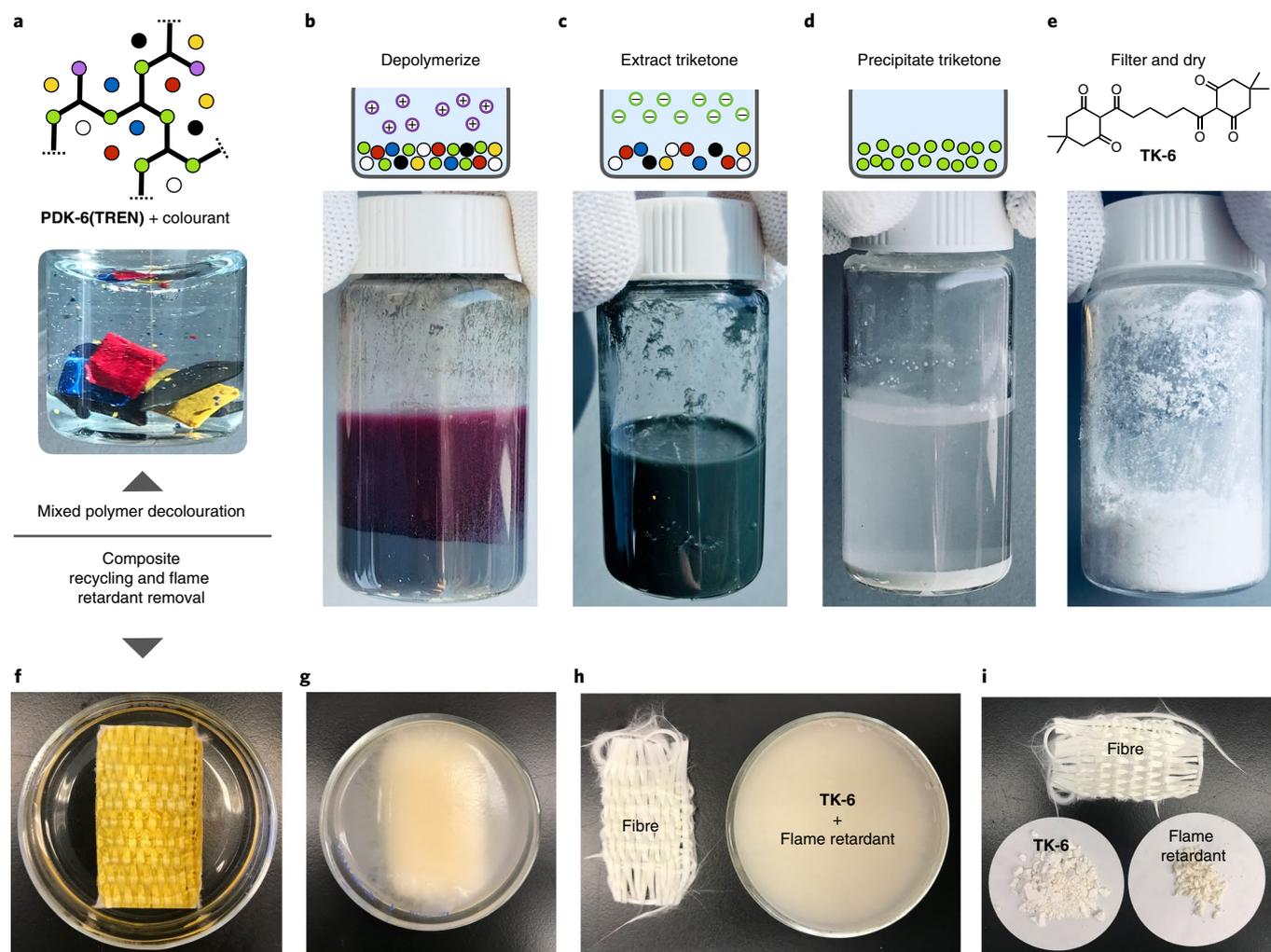


Fig. 4 | Mixed polymer decolouration, additive removal and closed-loop recycling of fibre-reinforced composites. **a**, A mixed-colour waste stream consisting of **PDK-6(TREN)** compounded with carbon nanofibres, TiO_2 , blue, yellow or red organic dyes. **b**, Red, blue, yellow and black samples of **PDK-6(TREN)** were completely depolymerized at room temperature in 5.0 M H_2SO_4 to yield a solid mixture of **TK-6** monomer and pigments/additives. **c**, **TK-6** was extracted into aqueous base at room temperature and separated from additives by filtration. **d,e**, The basic extract was acidified, precipitating pure **TK-6** monomer. **f**, Fibreglass cloth, impregnated with **PDK-6(TREN)**, containing 25% (wt/wt) TPP flame retardant. **g,h**, Depolymerization of **PDK-6(TREN)** enables separation and recovery of undamaged fibreglass cloth. **i**, **TK-6** monomer is separated from the flame retardant additive in aqueous base, allowing the fibreglass cloth, flame retardant and **TK-6** monomer to be isolated from each other.

sequence (depolymerize, extract and precipitate), allowing triketone, flame retardant and fibre-reinforcing fabric to be recovered (Fig. 4g–i). Specifically, the initial depolymerization of the PDK resin allows the fibreglass cloth to be removed as a single, undamaged component, leaving behind a mixture of **TK-6** monomers and TPP. The triketone monomer is separated from TPP by extracting it into the base and precipitating it using acid—effectively separating and isolating pristine fibre material, resin monomer and flame retardant (Fig. 4i).

Recovery of virgin-quality monomer enables upcycling. It's noteworthy that **TK-6** monomer obtained from each of the recycling experiments showed no detectable side products, residual amine, pigments or flame-retardant additives (Supplementary Figs. 10 and 11). The recovery of pure TK monomers enables immediate re-use for synthesizing new polymers of the same or different formulation, thus maximizing the inherent value of waste material. To demonstrate that recovered triketone monomers can be re-formulated into PDKs with the same or differentiated properties, we synthesized

PDK-6(TREN) from recycled **TK-6** as well as network polymers **PDK-6(TREN:ODA)** and **PDK-6(TREN:PPG)** using mixtures of TREN and 4,4'-dioxyaniline (ODA) or poly(propylene glycol) bis(2-aminopropyl ether) (PPG, $M_n = 2,000 \text{ g mol}^{-1}$), respectively (Fig. 5). Dynamic mechanical analysis (DMA) of recycled **PDK-6(TREN)** shows nearly identical properties to **PDK-6(TREN)** synthesized from pristine **TK-6** (Fig. 5b). The storage moduli (E') of re-formulated PDK materials range from $0.3(\pm 0.1) \text{ GPa}$ for **PDK-6(TREN:PPG)** to $1.8(\pm 0.2) \text{ GPa}$ for **PDK-6(TREN:ODA)** (Supplementary Fig. 11). Formulation chemistry whereby linear polymeric diamines are embedded into PDK networks further allows their ductility to be readily tuned: for example, incorporation of only 5 mol% poly(tetrahydrofuran) bis(3-aminopropyl ether) (M_w of $\sim 1,000 \text{ g mol}^{-1}$) into **PDK-10(TREN)** networks improved the toughness of PDKs without significantly sacrificing room-temperature storage and tensile moduli (Fig. 5d,e).

Dynamic covalent diketoenamine bond exchange with aliphatic and aromatic amines. The ability to formulate dynamic covalent

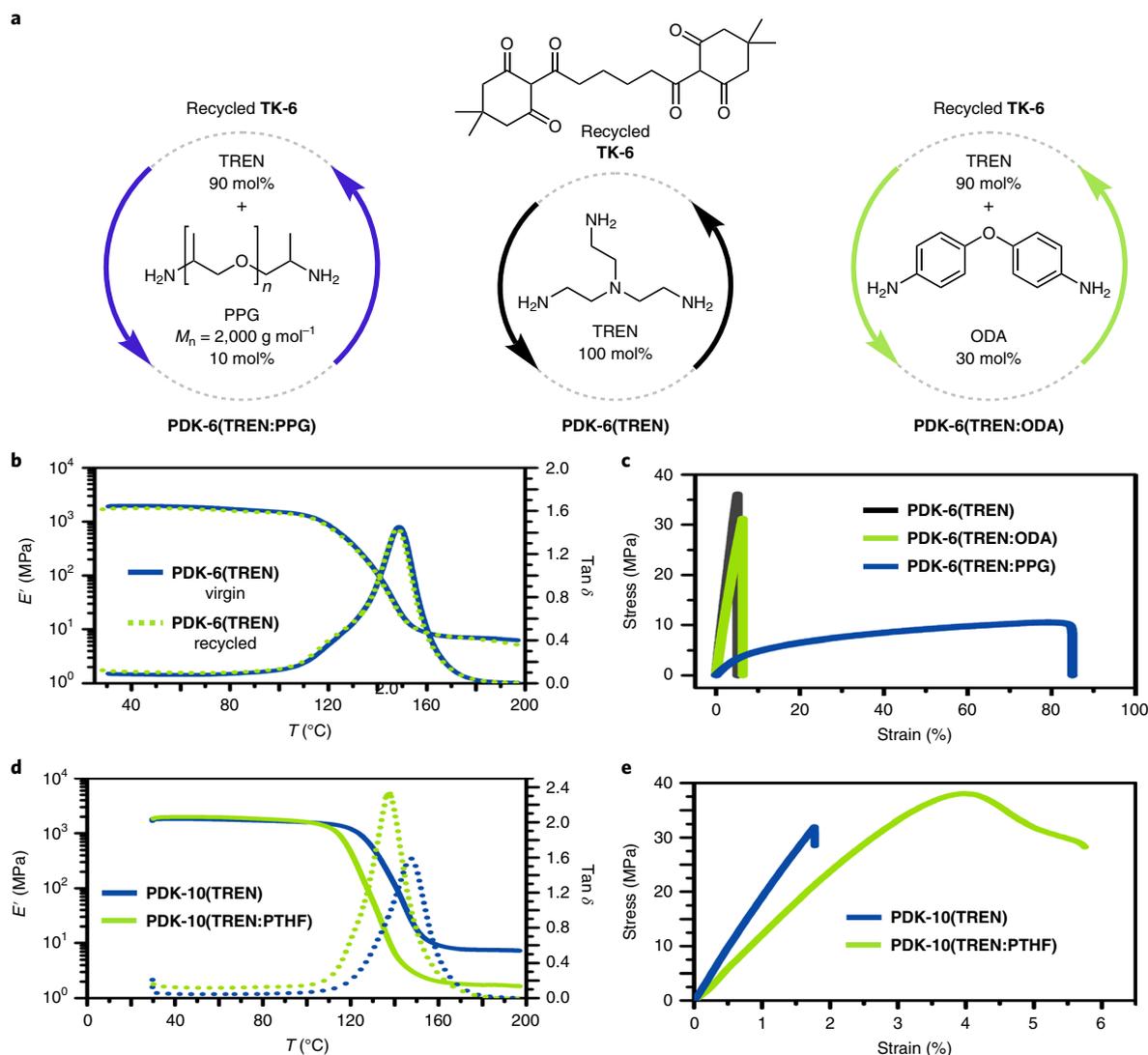


Fig. 5 | Re-formulation of PDK networks. **a**, TK-6 obtained through depolymerization of PDK-6(TREN) was used to re-formulate PDK networks with TREN, TREN alongside 4,4'-oxydianiline (ODA) and TREN alongside PPG. **b**, DMA of PDK-6(TREN) showed nearly identical properties when formulated from either virgin or recycled TK-6 monomer. **c**, Tensilemetry for PDK-6(TREN), PDK-6(TREN:PPG) and PDK-6(TREN:ODA). **d**, **e**, DMA showing E' (solid lines) and $\tan \delta$ (dotted lines) (**d**) and tensilemetry (**e**) for PDK-10(TREN) and PDK-10(TREN:PTHF) containing 5 mol% poly(tetrahydrofuran) bis(2-aminopropyl ether) (PTHF).

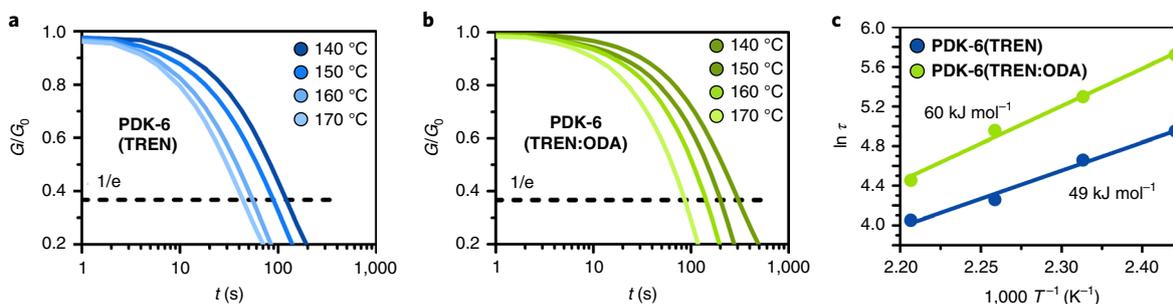


Fig. 6 | Dynamic covalent behaviour of PDK networks. **a–c**, Temperature-dependent stress relaxation for PDK-6(TREN) (**a**) and PDK-6(TREN:ODA) (**b**) polymers shows Arrhenius-type behaviour with activation energies (**c**) of 49 and 60 kJ mol^{-1} , respectively.

network polymers with both aliphatic and aromatic amine monomers is unusual, and a direct consequence of diketoenamine bond-exchange energetics³⁸. Kinetic analysis of the diketoenamine bond

exchange revealed remarkably low, catalyst-free activation energies for associative bond exchange: 29(± 0.9) kJ mol^{-1} for aliphatic amine exchange and 62(± 2) kJ mol^{-1} for aromatic amine (aniline)

exchange (Supplementary Figs. 13–15). We found that PDK network polymers containing both aliphatic and aromatic amines yield materials that reconfigure and relax with a temperature dependence that follows Arrhenius behaviour, consistent with PDKs being vitrimers²⁷. The temperature-dependent stress-relaxation behaviour for PDK-6(TREN) and PDK-6(TREN:ODA) shows activation energies of, respectively, 49 kJ mol⁻¹ and 60 kJ mol⁻¹ for solid-state bond exchange (Fig. 6).

Discussion

The closed-loop polymer life cycles enabled by PDKs contrast with those for conventional polymers, which are synthesized using irreversible bond-forming reactions that make it difficult and costly to recover the original monomers in high purity. Furthermore, while dynamic covalent polymers have been designed, in principle, around the ability to exchange bonds²⁷, examples of energy-efficient depolymerization and chemical separations to obtain immediately reusable monomers are exceedingly rare. Indeed, PDKs may be privileged in this regard. Specifically, our work provides an important counterpoint to the observed stability of poly(ketoenamine)s to acid-catalysed hydrolysis^{28,39–41}, showcasing the importance of the second keto functionality in re-directing the foundational behaviour of our materials toward more facile recycling, separation, re-manufacturing and re-use in a fully closed-loop fashion (Supplementary Fig. 1). As the global binge on plastics accelerates⁴², PDKs stand out among a growing class of smarter plastics designed for chemical circularity.

Data availability

The authors declare that the data supporting the findings of this study are available within the paper and its Supplementary Information, and also from the authors upon request. Crystallographic data for compounds **3**, **5** and **TK-6** are available free of charge from the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk) under reference nos. 1891131, 1891132 and 189113, respectively.

Received: 17 May 2018; Accepted: 1 March 2019;
Published online: 22 April 2019

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Acknowledgements

The technical scope of this work was supported by the Laboratory Directed Research and Development Program of Lawrence Berkeley National Laboratory under US Department of Energy contract no. DE-AC02-05CH11231. K.E.L. was supported by the US Department of Energy, Office of Science, Office of Workforce Development for Teachers and Scientists (WDTS) under the Science Undergraduate Laboratory Internship (SULI) programme. Portions of this work, including organic and polymer synthesis and characterization, were carried out as a User Project at the Molecular Foundry, which is supported by the Office of Science, Office of Basic Energy Sciences, of the US Department of Energy under contract no. DE-AC02-05CH11231.

Author contributions

B.A.H. and P.R.C. designed and planned the project. P.R.C. synthesized and characterized all PDK materials and their recyclability. A.M.S. synthesized small molecules and carried out experiments to measure the activation energies for amine exchange. K.E.L. carried out experiments to characterize the extent of network formation by ball-milling. B.A.H. and P.R.C. wrote the manuscript, with contributions from all co-authors.

Competing interests

B.A.H. and P.R.C. are inventors on US 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.

Additional information

Supplementary information is available for this paper at <https://doi.org/10.1038/s41557-019-0249-2>.

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