Sharing sustainability perspectives enabled by advances in dynamic covalent chemistry from the Center for Plastics Innovation, University of Delaware, Newark, Delaware, USA.

Circularity in polymers: addressing performance and sustainability challenges using dynamic covalent chemistries

Dynamic polymeric materials are uniquely positioned to enable plastics waste reduction thanks to chemical innovations, advances in thermomechanical models, and the emergence of economic and environmental assessments of materials circularity. This review presents a multidisciplinary overview of the challenges and opportunities towards the design of sustainable and recyclable macromolecular materials for a circular economy via advances in dynamic covalent chemistry. Cover artwork was created by Kelly Walker.

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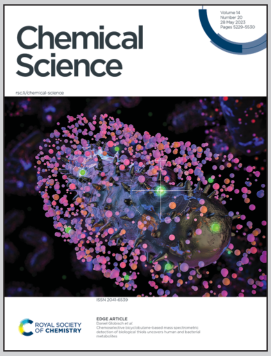

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Circularity in polymers: addressing performance and sustainability challenges using dynamic covalent chemistries

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The circularity of current and future polymeric materials is a major focus of fundamental and applied research, as undesirable end-of-life outcomes and waste accumulation are global problems that impact our society. The recycling or repurposing of thermoplastics and thermosets is an attractive solution to these issues, yet both options are encumbered by poor property retention upon reuse, along with heterogeneities in common waste streams that limit property optimization. Dynamic covalent chemistry, when applied to polymeric materials, enables the targeted design of reversible bonds that can be tailored to specific reprocessing conditions to help address conventional recycling challenges. In this review, we highlight the key features of several dynamic covalent chemistries that can promote closed-loop recyclability and we discuss recent synthetic progress towards incorporating these chemistries into new polymers and existing commodity plastics. Next, we outline how dynamic covalent bonds and polymer network structure influence thermomechanical properties related to application and recyclability, with a focus on predictive physical models that describe network rearrangement. Finally, we examine the potential economic and environmental impacts of dynamic covalent polymeric materials in closed-loop processing using elements derived from techno-economic analysis and life-cycle assessment, including minimum selling prices and greenhouse gas emissions. Throughout each section, we discuss interdisciplinary obstacles that hinder the widespread adoption of dynamic polymers and present opportunities and new directions toward the realization of circularity in polymeric materials.

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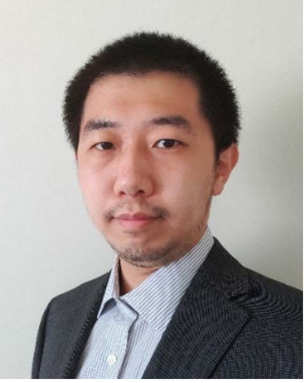

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Introduction

Polymeric materials are indispensable in modern society due to their high strength-to-weight ratio and durability.[1] Over the past ∼70 years, plastics use and production have outgrown those of most other man-made materials, such as cement and steel,[2,3] and ∼390 million tons of plastics were produced globally in 2021.[4] That amount is expected to grow exponentially over the next 30 years under various production scenarios.[4,5]

Accompanying this rapid growth of plastics are the negative global impacts derived from the linear economy model, in which raw materials are collected, transformed into products, and eventually discarded as waste.[6] Additionally, the majority of plastics production consumes non-renewable natural resources, and the current handling of post-consumer products results in further resource depletion,[7,8] waste accumulation,[9] and environmental (micro)plastics contamination.[10–12] In response to these concerns, efforts have intensified to generate a more circular, closed-loop plastics consumption model.[13] Within the closed-loop framework, one approach to minimize virgin resource input and waste accumulation is to adopt a reduce, reuse, remanufacture, and recycle system (Fig. 1).[13–16]

Although achievable in principle,[17–21] several critical challenges prevent fully closed-loop circularity for polymer plastics waste.[22–25] For example, thermosets (*e.g.*, epoxy resin, vulcanized rubber) comprise ∼20 wt% of manufactured polymeric materials and are generally considered unrecyclable.[26–28] The permanently crosslinked architecture of thermosets imbues these materials with solvent resistance and increased mechanical robustness; however, this structure also eliminates the ability to reprocess the networks *via* most mechanical or chemical means.[27,29] Thus, thermoset-based polymers are typically landfilled.[26,30] In contrast, thermoplastics (*e.g.*, plastic bottles, films) are considered more recyclable using the aforementioned approaches.[31] In thermoplastics, polymer chains associate mainly by intermolecular forces and can flow at elevated temperatures, yet polymer chains can irreversibly cleave or crosslink during mechanical recycling.[22,32] The addition of virgin polymer is required to regenerate products with comparable properties to the original polymeric materials, which undermines full circularity.[14,22]

Another major obstacle to the circularity of polymeric materials is the unfavorable cost of recycling *vs.* virgin feedstock production.[16] This high cost, present in both mechanical and chemical recycling, is the result of multiple factors, including waste collection, sorting, and total energy consumption.[33] For example, sorting is necessary to separate different plastics and avoid significant property reduction of mechanically-recycled materials as a result of mixed waste.[20,34] During chemical recycling, additives and impurities in real plastics waste also can adversely affect catalyst activity, decreasing process efficiency and increasing total energy demand.[22,35–40] These recycling costs are rarely recovered in the value of recycled materials, leading to low recycling rates of plastics (*e.g.*, 10 wt% for high-density polyethylene (HDPE), 5 wt% for low-density polyethylene

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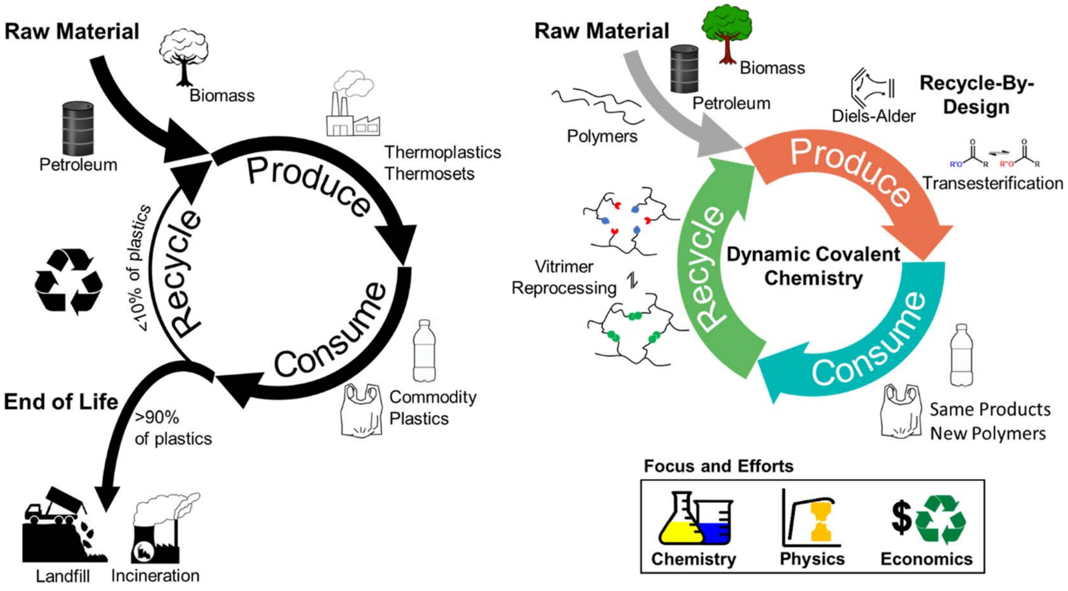


Fig. 1 The circularity challenge. (Left) Conventional recycling efforts result in less than 10 wt% of plastics being recycled and over 90 wt% of plastics being landfilled or incinerated. Commodity plastics and plastic products are produced from petroleum- and bio-based feedstocks; however, challenges in conventional recycling processes limit full circularity. Recycling rates are illustrated by a thinner recycling arrow *vs.* end of life. (Right) Closed-loop circularity realized by dynamic covalent chemistries leads to increased retention of plastics in the production and consumption cycle. Polymeric materials are designed for specific recycling conditions through dynamic covalent chemistries, such as Diels–Alder and transesterification. Feedstocks can include petroleum, biomass, and existing commodity polymers. The same plastic products are produced using the new dynamic covalent chemistry-based polymers and reprocessed through reversible bond-breaking and reforming. Interdisciplinary efforts, including an expanded suite of available chemistries, structure–property relationships, and economic/environmental assessments, are still needed to realize the widespread implementation of dynamic covalent chemistry in closed-loop circularity.

(LDPE), less than 1 wt% for polystyrene (PS), polypropylene (PP), or poly(vinyl chloride) (PVC) in the U.S.),[41,42] motivating the need for innovative recycling strategies.

Dynamic covalent chemistry (DCvC) in polymeric materials provides a synthetic pathway to address circularity challenges, including unrecyclable networks and irreversible chemical changes (Fig. 1).[21,43,44] The characteristic high reversibility and stimuli-responsiveness of DCvC[45–47] permit bond breaking and reforming during the recycling of corresponding modified polymeric networks (*e.g.*, dynamically-crosslinked epoxy resins),[48,49] unlike conventional thermosets. Furthermore, the irreversible structural changes and subsequent property deterioration from conventional recycling approaches can be mitigated or even circumvented by DCvCs. For example, industrially recycled poly(ethylene terephthalate) (PET) suffers from property deterioration (*e.g.*, after 2 cycles, the melt viscosity decreased by 50%) due to thermal and shear degradation during the extrusion process,[16,50] whereas a DCvC-modified PET with reconfigurable ester linkages displays reprocessability with minimal mechanical property loss over 3 cycles.[51,52] Finally, DCvC can reduce recycling costs associated with reprocessing conditions, separations, and end-product valorization. The bond activity and tunable nature of DCvCs allow polymeric materials to be recycled at lower temperatures (*e.g.*, sterically hindered urea bonds and alkoxyamine can lower the reprocessing temperatures of corresponding materials from over 140 °C to less than 40 °C), decreasing energy requirements.[53–56] Beyond thermal reprocessing, DCvC provides opportunities to recycle plastics *via* selective dissolution and/or depolymerization under mild conditions. For example, a boroxine-crosslinked polymer is recoverable *via* depolymerization in an ethanol/*N*-methylpyrrolidone (NMP) solvent mixture at 30 °C, but remains suitable for many applications due to its mechanical strength, thermal stability, and hydrophobicity.[57–59] The tunability of DCvC allows for potential implementation within current industrial manufacturing processes, leading to reduced investment in additional infrastructure.[60,61] In some cases, DCvC incorporation has even been shown to improve select material properties (*e.g.*, chemical sensing, shape memory effects),[44,62] adding value to offset the recycling costs.[63]

Although the implementation of DCvC in polymeric materials is promising, there remain practical challenges (*e.g.*, processing condition development, cost) before this strategy can be extended to the broad range of applications and recycling conditions inherent to polymer production. The synthetic design of DCvC for incorporation into polymeric materials must tailor properties to fit industry-level (re)processing requirements,[44] such as fast stress relaxation[64] and robustness, after repeated recycling.[65] The balance between dimensional stability during application and material flow during reprocessing in dynamic polymeric materials is a challenge as the overall relaxation rates are dictated by DCvC bond reconfiguration and polymer chain motion.[47] Thus, a fundamental understanding of structure–property relationships and physical models for DCvC-based polymers is necessary to predict performance and to develop appropriate (re)processing conditions to enable circularity.[66] To align academic advances with wide-scale adoption, the generation of required data sets (*e.g.*, reprocessing temperatures, performance after multiple cycles, relevant reagents) is pivotal but currently limited.[22] Techno-economic analysis (TEA) and life-cycle assessment (LCA) will be critical to evaluate the costs and environmental impacts during the production/recycling processes of DCvC-containing polymers.

In this review, we describe the role and associated challenges of DCvCs in the development of closed-loop, recyclable polymer materials. Many reviews highlight synthetic advances in DCvCs and dynamic polymers;[67–71] thus, that topic is not extensively covered herein. Instead, we focus on the application of these motifs towards circular polymers. First, we briefly summarize the key features of DCvCs and examine how each feature can be leveraged to promote the circularity of polymeric materials. Next, we outline the advantages and challenges in DCvC for both recycle-by-design polymers and existing commodity polymers. Then, we discuss the thermomechanical properties that impact dynamic covalent polymers from the perspective of their underlying polymer physics, which can guide the design and optimization of recycling processes. Finally, we highlight the practical limitations and opportunities toward the implementation of dynamic covalent chemistries in the circular economy using elements derived from economic and environmental studies (TEA and LCA), including minimum selling price and greenhouse gas emissions. By considering all facets of DCvC-containing polymer recycling, we provide a more comprehensive viewpoint on enhancing the circularity of polymeric materials.

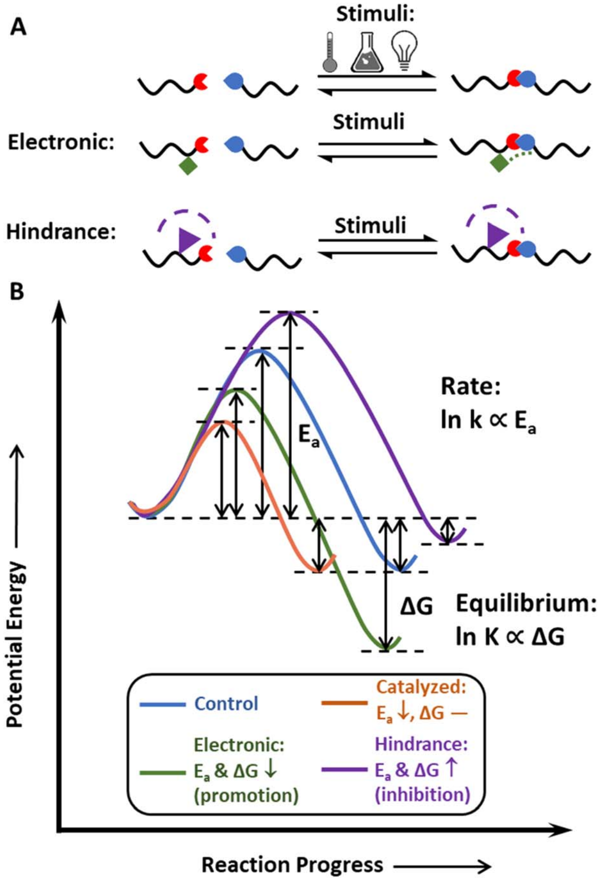


Fig. 2 (A) Generic dynamic covalent chemistry scheme related to equilibrium control through electronic/steric effects. (B) Control of reaction equilibrium and rate (rate constant: *k*) *via* steric hindrance and electronic effects. Blue: control. Orange: catalyzed. Green: electronic effects (promote the reaction in this case). Purple: steric effects (inhibit the reaction in the case shown in (A)).

Dynamic covalent chemistry for polymeric material design

The concept of dynamic covalent chemistry was described by Rowan *et al.* in 2002,[45] as an extension of supramolecular chemistry to the covalent level. DCvC proceeds by the equilibration process of bond breaking and reforming, which leads to the efficient formation of products under thermodynamic control.[45] At the molecular level, these bonds undergo reversible exchange without unwanted side reactions,[45] making DCvC attractive in many arenas, including drug delivery,[72,73] robotics,[44,74] sensors,[75,76] and recycle-by-design polymers.[21,77,78]

In general, dynamic bonds are designed with three key properties in mind: thermodynamic reaction equilibrium, reaction rate, and stimuli-responsiveness (Fig. 2). The reaction equilibrium defines the reversibility of the bond, and the equilibrium constant, K, is exponentially proportional to the change in free energy upon product formation, or ΔG. Structural design strategies (*e.g.*, altering steric hindrances,[53] electronic effects[79]) can tune this equilibrium, providing pathways to develop additional DCvC reactions and modulate the dimensional stability of the resulting material in corresponding applications. One example is the use of a hindered urea bond to alter the equilibrium of C–N bonds in polyureas and poly(urethane-ureas).[53] Although an unmodified urea bond is quite stable, the hindrance imposed on the nitrogen atom by bulky alkyl groups weakens the C–N bond by disturbing the coplanarity and conjugation effect of the carbonyl and amine groups, resulting in reversible, dynamic urea bonds[80] and leading to reprocessable networks crosslinked by these bonds.[81] In another illustration of the impact of equilibrium on material properties, imine-based dynamic covalent networks exhibited improved water-resistance due to the conjugative effect of C=N–X structures *via* the incorporation of electron-withdrawing functionalities,[79,82,83] yet also maintained good recyclability *via* dynamic bond exchange in solution.[84]

Reaction equilibrium indicates the tendency of dynamic bonds to exchange, whereas reaction rate determines the time required for these bonds to rearrange. To display dynamic features on the macroscopic level, the reversible reaction must achieve equilibrium within a relevant timeframe (*e.g.*, $10–10^3$ s for common molding procedures) after exposure to an environmental stimulus.[66,85] The reaction rate and reprocessing time of a dynamic polymer reflect the mechanism and kinetics of the specific DCvC, denoted by the activation energy, E_a (Fig. 2B).[86,87] Some DCvCs are intrinsically fast with a relatively low E_a. For example, under mild temperatures (*e.g.*, below 100 °C), the Diels–Alder (D–A) reaction (E_a ~50 kJ mol^{-1})[84] and boroxine exchange reactions (E_a ~80 kJ mol^{-1})[88,89] can lead to the complete reconfiguration of recyclable covalent networks within an hour without the aid of catalysts.[86,87] Unlike the D–A and boroxine reactions, some of the DCvC networks exchange slowly with a high energy barrier, such that a catalyst is often necessary to lower the E_a and dramatically accelerate the reaction.[90] Transesterification is an example of DCvC that is heavily dependent on both the catalyst type and the relative amount of catalyst present, as the relaxation time can be lowered to more desirable timescales for reprocessing (*e.g.*, 10–10^3 s).[90] In transesterification, the high reaction rate (and short relaxation time) achieved by optimizing the conditions and catalyst choice can facilitate reprocessing/recycling using methods, such as melt extrusion and injection molding.[51,91] Therefore, the reaction rate dictates the framework for throughput, application conditions, available processing techniques,[91] and related logistics associated with the dynamic polymer recycling processes.

Finally, tailored responsiveness with respect to specific stimuli, including heat, light, pH, and others, can lead to a range of responsive behavior in different environments. For example, heat is commonly used in dynamic covalent polymer recycling. As indicated by the Maxwell relations and Arrhenius equations,[92] increasing the temperature accelerates both sides of a reversible reaction but often shifts the equilibrium towards dissociation, which promotes DCvC network reprocessing (*e.g.*, D–A reaction).[93] pH-responsive DCvCs can enable selective depolymerization under acidic or basic environments (*e.g.*, hemiaminal,[94] imine[84]) in mixed plastics,[57–59] providing an alternative chemical recycling pathway to reduce sorting costs. Although light has not been widely used in recycling, some DCvCs facilitate rapid healing under UV irradiation (*e.g.*, disulfide exchange),[95] potentially supporting circularity by extending the product lifetime and reprocessing pathways that utilize this responsiveness.[96] Conversely, in the absence of a triggering stimulus, the materials are highly stable and exhibit high creep resistance.[92]

Overall, reversibility, high reaction rates, and stimuli-responsiveness are essential starting points to achieve the circularity of polymeric materials *via* functionalization with dynamic covalent chemistries. Although macromolecular circularity requires long-term and iterative optimizations in both academic research and industrial practice, dynamic covalent chemistry, in principle, has the potential to facilitate the strategic, recycling-oriented design of polymeric systems. Therefore, it is imperative to develop a more comprehensive understanding of the chemistry (*i.e.*, synthetic routes), physics (*i.e.*, physical models), and industrial (*i.e.*, economic and environmental impacts) perspectives through the lens of closed-loop recyclability.

Synthetic progress in DCvC-containing polymers

In general, recent synthetic advances related to DCvC in polymer recycling can be classified into two categories: polymer construction from functional monomers (*i.e.*, recycle-by-design) and post-polymerization modification. Recycle-by-design focuses on inherently circular polymers at the point of invention whereas post-polymerization addresses challenges related to existing polymer waste. For example, epoxy resins and polyurethanes can be cured with crosslinkers that utilize DCvC (*e.g.*, transesterification,[97] Diels–Alder reaction[98]).[99–102] Similarly, it is feasible to introduce DCvC into other common polymers, such as poly(meth)acrylate, polyolefins, polystyrene, and polydiene networks, *via* synthetic approaches from monomers and post-polymerization modification.[48,81,103–106] Although both methods target a recyclable polymer product, they each have their own set of advantages, challenges, and opportunities.

Recycle-by-design

Polymers synthesized with dynamic chemistries in mind comprise a significant portion of the research in the field. By modulating the molecular design of polymeric materials, chemists gain control over the dynamic properties of the system. This strategy enables the tuning of polymer architecture, bond equilibrium (*i.e.*, reversibility), or stimuli response towards desired properties in a manner that offers more synthetic control than DCvC post-modification of existing polymers. Though this recycle-by-design approach results in a myriad of inherently recyclable polymers, it often is accompanied by a series of shortcomings (*e.g.*, slow reaction rates, loss of crosslink density) that result in significant challenges related to scale up for specific applications.

Numerous synthetic routes towards overcoming these challenges have been investigated since Leibler and collaborators proposed the concept of vitrimers in reprocessable epoxy resins.[97] In their ground-breaking study of dynamic covalent networks,[97] a diglycidyl ether of bisphenol A (DGEBA) was cured with carboxylic di- and tri-acids in the presence of two zinc catalysts to form the resultant network (Fig. 3). These vitrimers consisted of an associative network of ester linkages that broke and reformed concurrently, theoretically maintaining crosslink density (as opposed to dissociative reactions in which the linkage breaks first and a new linkage forms second). The networks exhibited reprocessability through compression molding at 240 °C within 3 min with comparable tensile strength and strain-at-break to the initial polymers.[97] However, the reprocessed epoxy materials still displayed a slight decrease in Young's modulus,[97] indicating a loss of crosslink density in the recycled networks. Additionally, estimations of the DCvC activation energy suggested that relaxation at room temperature would occur on the order of a few years, threatening the long-term dimensional stability of the material.[97] In total, this initial investigation both established the opportunities in using DCvC in polymer networks and highlighted key limitations associated with these initial DCvC-based polymeric materials, (*e.g.*, high reprocessing temperature requirements, property loss, creep) (Fig. 4).

Accelerating reaction rates through catalysis and molecular design. As discussed above, the rate of bond exchange is pivotal for promoting the circularity of these polymeric materials. One possible approach to accelerate the reaction is to utilize high

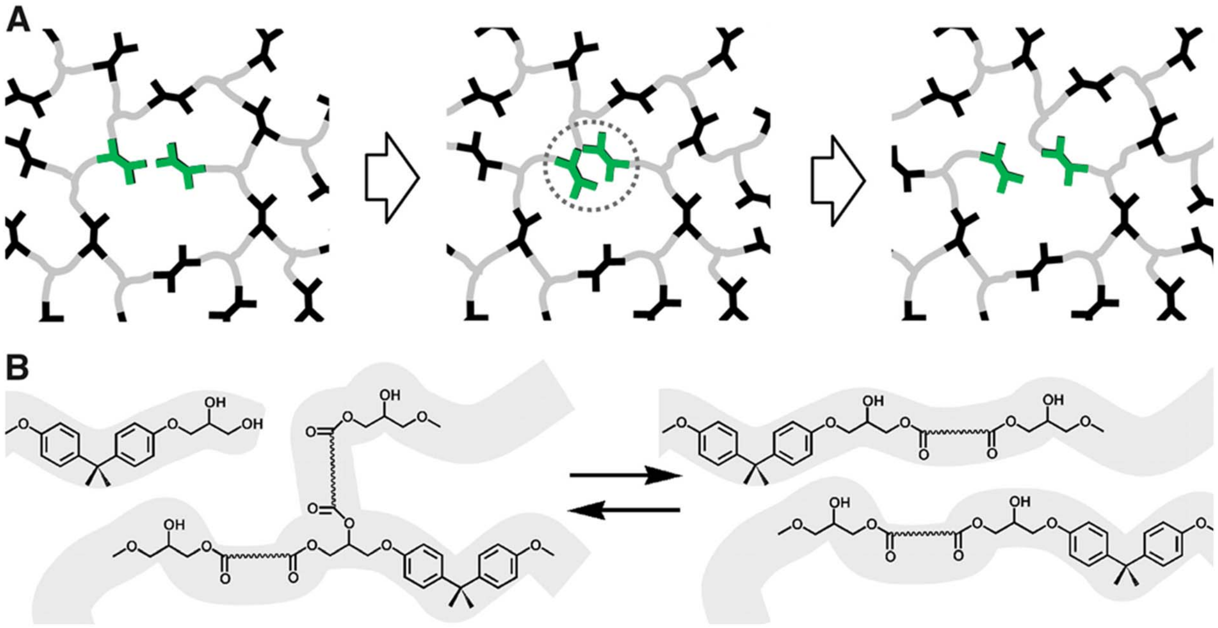


Fig. 3 Rearrangement of reprocessable epoxy networks. (A) Schematic of a network with associative exchange processes (highlighted in green) that do not require depolymerization or loss of crosslink density. (B) Chemical illustration of a transesterification exchange process in hydroxy-ester networks. Adapted from ref. 97 with permission from the American Association for the Advancement of Science, copyright 2011.

temperatures for reprocessing, as illustrated in the previous example.[97] Yet, high operating temperatures necessitate increased energy consumption and decreased compatibility with various polymer matrices.[107] An alternative pathway to enhance the exchange rates of DCvCs is to optimize catalyst type and loading.[100,108–111] New and highly reactive zinc catalysts have enabled more efficient dynamic exchange and reprocessing in ester networks.[97,102,112,113] To extend the scope of recyclable epoxy-based polymers *via* dynamic transesterification, other catalysts, such as tin and organic Lewis bases, have been implemented, and similarly, facilitated reprocessing over several cycles.[100,108–111] For example, replacing the zinc catalyst in

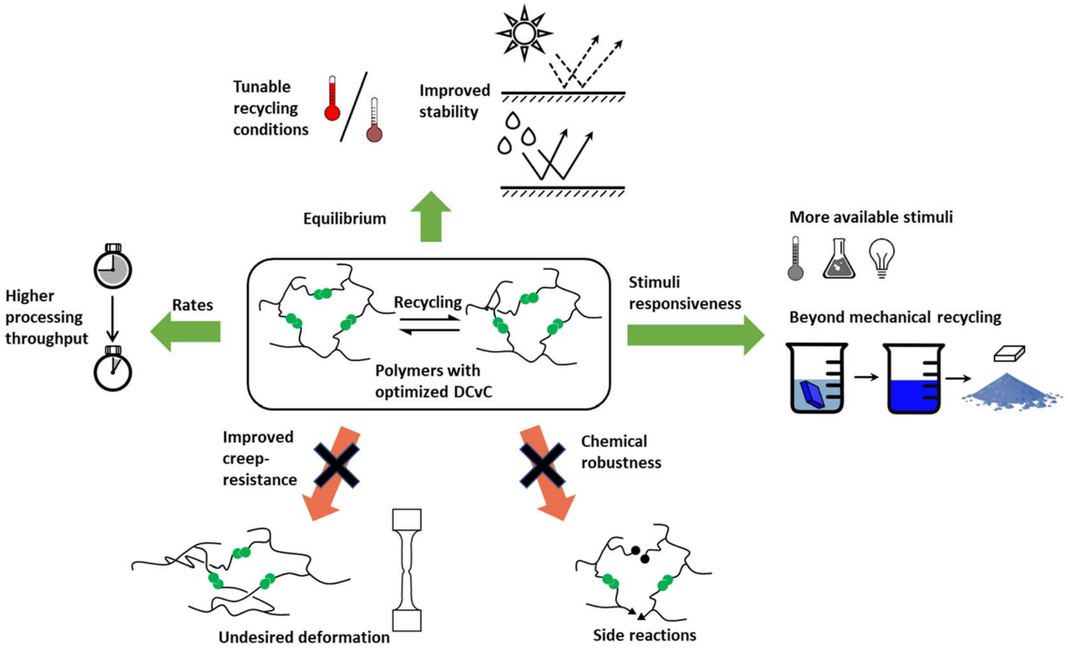


Fig. 4 Achievable improvements in recyclable dynamic networks *via* recycling-by-design strategy. Optimized DCvC-containing polymeric materials can exhibit tunable recycling conditions, fast (re)processing, various recycling approaches, and improved stability against side reactions or undesirable deformation.

a reprocessable epoxy resin with 1,5,7-triazabicylo[4.4.0]dec-5-ene decreased the reprocessing temperature by 70 °C (from 240 °C to 170 °C) with a reprocessing time of 10 min.[97,100]

Aside from catalyst design, catalyst loading also affects reprocessing conditions, although it does not influence the activation energy of the dynamic exchange. For instance, increasing the catalyst amount from 1 mol% to 5 mol% has been shown in some cases to decrease the stress relaxation time by approximately one order of magnitude, which subsequently decreases the reprocessing time.[114] Albeit a promising route to tailor relaxation times, economic considerations also must be taken into account during catalyst selection to balance projected cost with returns on material property improvement. Using the previous example, it is important to evaluate whether the cost to increase catalyst loading from 1 mol% to 5 mol% (*i.e.*, the cost of the catalyst itself) is offset by the expected value returned by a lower overall reprocessing time.

In addition to potential hurdles related to catalyst cost, concerns have been raised regarding catalyst compatibility, catalyst leaching, and environmental impacts.[90] These issues have motivated researchers to design catalyst-free vitrimers by inserting catalyzing functional groups directly into the dynamic covalent polymer.[115,116] When the inserted species are incorporated in close proximity to the reaction center (Fig. 5A), this effect is referred to as neighboring group participation (NGP).[64,117–119] For example, catalyst-free dynamic ester exchange was achieved *via* the engagement of a neighboring acid group close to the transesterification center. This structural modification resulted in the formation of transient cyclic anhydrides and free alcohols, enabling a dissociative dynamic exchange.[115] Expanding upon this phthalate monoester mechanism, Du Prez and collaborators introduced a tertiary amine on the beta position of the hydroxyls (Fig. 5B),[64] further decreasing the relaxation times by a factor of 500 through a dual NGP mechanism (relaxation times, $\tau^* \sim 1$ s below 160 °C).[64] The resultant fast exchange and relaxation time enabled the reprocessing of chopped samples through industrially relevant processing techniques (*e.g.*, extrusion), which is a promising improvement for physical recycling at scale.[64,91] A recent publication reported an alternative NGP transesterification *via* beta-keto activated exchange instead of neighboring acid and amine participation, allowing 5 cycles of consecutive remolding at mild conditions (*e.g.*, 70–100 °C).[120] The concept of NGP also has been introduced to optimize other DCvCs to expand the reach of recycling conditions for related materials. For example, the incorporation of a neighboring tertiary amine accelerated the boronic ester exchange by five orders of magnitude.[87] Yet another study integrated NGP-assisted silyl exchange into DCvC-modified polystyrene, increasing the reaction rate by three orders of magnitude and decreasing the corresponding reprocessing temperature by 30 °C.[121] In general, these NGP approaches are a promising direction for significant rate enhancements in DCvCs while reducing the need for small-molecule catalyst additives.[117]

When incorporating the above strategies to accelerate DCvC reactions, the trade-off between exchange rates and material performance needs to be considered. Faster exchange rates in DCvC-based polymeric materials can facilitate reprocessing but also lower the upper limit of operating conditions under which the material will maintain mechanical integrity. The latter negatively impacts the application potential, particularly in high-performance thermoset materials expected to function in harsh environments (*e.g.*, elevated temperatures, high mechanical stress).[22,44,122] DCvC-based material designs that balance reprocessing conditions and target uses are crucial to enabling circularity without affecting performance.

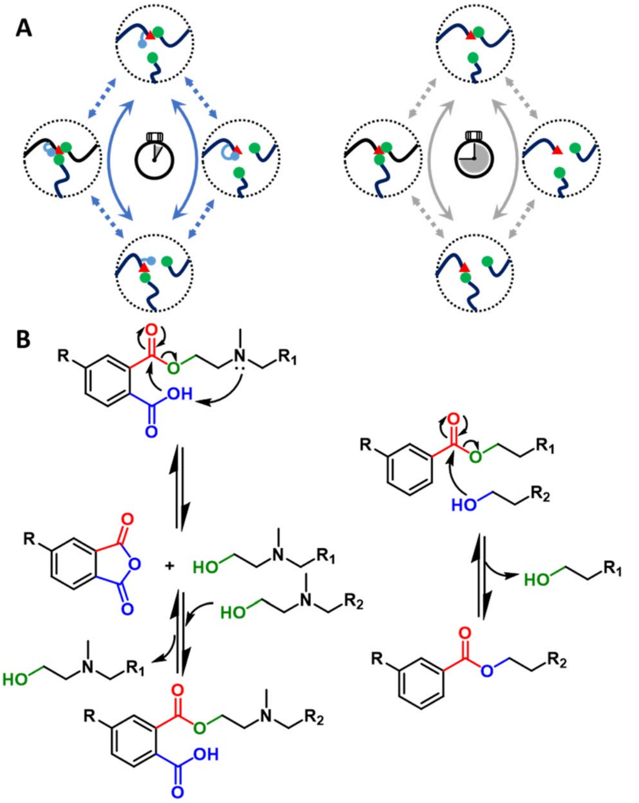


Fig. 5 (A) General NGP-assisted mechanism of DCvC (left). Non-NGP mechanism of DCvC (right). (B) Proposed NGP mechanism for rapid transesterification (left). Non-NGP transesterification (right).

Approaches for creep resistance in recyclable systems. Maintaining dimensional stability under operating conditions in recyclable, DCvC-based polymeric materials requires complementary approaches that specifically target reprocessability and creep resistance.[96] One strategy to enhance the creep resistance of dynamically crosslinked networks is to suppress the undesired bond exchange by increasing the DCvC E_a. According to the Arrhenius equation, a higher E_a of these reactions results in stronger temperature dependence and narrower temperature windows for activation of the corresponding DCvC.[96] For example, alkoxyamine chemistry is a well-known, dynamically reversible reaction with a high activation energy (up to 120 kJ mol^{-1}).[62,123,124] As a result, an alkoxyamine-modified rubber network that was fully reprocessable at 140 °C behaved as a permanently crosslinked network even at elevated temperatures, displaying limited creep (0.14% at 80 °C after 2 h). Similarly, bis(dialkylamino) disulfides ($R_2NS\text{-}SNR_2$)

exhibited an activation energy of 110 kJ mol^{-1}, resulting in minimal creep at higher temperatures (0.07% at 70 °C after 13.9 h) as well as a steep temperature dependence (0.07% at 70 °C, 1.9% at 100 °C, and 12.5% at 130 °C after 13.9 h).[103]

Another pathway to suppress creep is to introduce an appropriate level of permanent crosslinking.[47,125,126] In one study, crosslinked networks containing various fractions of dynamic boronic esters and irreversible linkages demonstrated that stress relaxation and creep can be moderated by the addition of permanent crosslinks that lend increased structural integrity.[125] A hybrid network with ~80 mol% permanent crosslinks suppressed the relaxation yet still permitted repeated healing.[125] In another system, an epoxy resin crosslinked *via* dynamic transesterification incorporated 40 mol% of thiol-epoxy permanent crosslinks into the network. The relaxation time of the vitrimer almost doubled, and creep was reduced by 65–71%, yet the material maintained full reprocessability *via* hot pressing.[47]

It is also possible to inhibit creep *via* combinational strategies of DCvC modification and non-covalent interactions. For example, a synergistic effect was achieved in a system of vitrimers featuring dynamic imine exchange with integrated metal-complexes.[127] Adding 5 mol% of metal ions to coordinate with flexible imine bonds induced further crosslinking of the vitrimer *via* non-covalent bonding and simultaneously doubled the activation energy of dynamic imine exchange (107.3 kJ mol^{-1} *vs.* 52.3 kJ mol^{-1}). This combined approach enhanced the creep resistance by raising the initial creep temperature by 60 °C (from 60 °C to 120 °C, Fig. 6).[127]

Tuning equilibrium towards improved stability and reprocessability. In addition to long-term dimensional stability, recyclable polymeric materials must maintain reprocessability, healability,[54,55] stability,[79] and strength during use.[53] By tailoring the equilibrium of a DCvC-based system, the resultant material can be constructed to enhance one or more of these properties. One example is the stabilization of imine bonds by electronic conjugation.[128] The dynamic imine bond is known to dissociate in the presence of water; however, the equilibria of imine exchange and solvolysis are influenced by neighboring N or O atoms (*e.g.*, hydrazone, acyl hydrazone, oxime),[79] facilitating control over reversibility.[79] Therefore, in an effort to improve the water-resistance of imine-based dynamic covalent resins, conjugated oxime bonds (33 mol%) were introduced into the networks. The oxime-modified vitrimers demonstrated improved structural integrity in the presence of water, with reduced 24 h water uptake (weight gain of ~1% *vs.* ~48%) when compared to unmodified networks.[84] Moreover, the oxime-modified imine vitrimers maintained their mechanical performance and chemical recyclability.[84]

Tailoring the equilibrium also plays an important role in reprocessing conditions for DCvC-based polymers. For example, the homolysis temperature of alkoxyamine C–ON bonds can be adjusted from 140 °C[124] to as low as 15 °C [54,55] by leveraging the electron-withdrawing effect of neighboring substituents. With an appropriate molecular design to shift the equilibrium, it is even possible to convert a non-dynamic reaction into a DCvC that displays reprocessability under mild conditions.[53] A well-known example is the hindered urea bond. A conventional urea bond is stable, but sterically hindering and twisting the C(O)–N bond facilitates dynamic dissociation and reconstruction.[53] Inspired by the facile amidolysis of bulky amides, Cheng and collaborators measured the equilibrium constants and rate constants of urea bond dissociation with different bulky amines.[53] By adjusting the bulkiness of the amines, the equilibrium constants varied by up to six orders of magnitude.[53] Among the investigated amines, a secondary amine containing a *tert*-butyl urea group displayed a moderately reversible equilibrium constant (7.9×10^5 M^{-1}) and a non-negligible dissociation rate (0.21 h^{-1} at 37 °C), indicating balanced bond stability and exchange rate.[53] A crosslinked poly(urethane-urea) gel containing hindered urea bonds on the main chain was prepared with a diisocyanate, a bulky diamine, and polyol

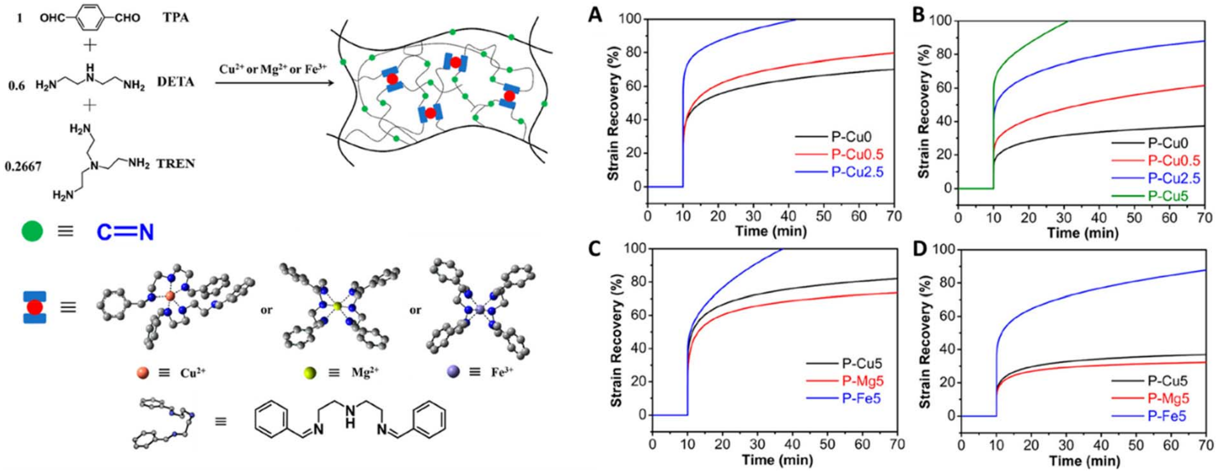


Fig. 6 (Left) Polyimine–metal complex vitrimers synthesized from terephthaldehyde (TPA), diethylenetriamine (DETA), and tris(2-aminoethyl) amine (TREN). (Right) Strain recovery curves to show the creep response of the polyimine–metal complex vitrimers at (A) 60 °C, (B) 80 °C, (C) 100 °C, and (D) 120 °C. Adapted from ref. 127 with permission from the American Chemical Society, copyright 2020.

crosslinkers (Fig. 7).[53] Self-healing (*i.e.*, the failure strain recovered to 50% at 1 h, 87% at 12 h) was achieved at 37 °C. The results revealed the importance of manipulating equilibrium as a powerful tool in designing circular polymeric materials *via* facile adjustment of chemical structures.[53]

Cheng's work on self-healing poly(urethane-urea) gels inspired a series of recyclable polymeric networks that leverage the bulkiness of the amines to tune polymer backbone chemistry.[81,129] A recent report highlighted the application of this hindered urea bond in a recyclable PMMA-based material.[81] The PMMA-based network was crosslinked by a hindered urea-functionalized dimethacrylate and then reprocessed for three cycles to yield homogeneous films. The recycled material showed no decrease in gel content (>99%) and no significant change in tensile storage modulus, suggesting recovery of crosslink density.[81]

Limiting side reactions to maintain mechanical integrity. Even with these highly engineered dynamic bonds, a large number of recyclable dynamic polymers experience diminished mechanical integrity or reduced crosslink densities after a few cycles of reprocessing.[102,130,131] Although the recyclability of these polymers has been improved significantly in comparison to existing plastics, this loss poses limits to full circularity as the ultimate goal. One main reason for the irreversible failure of recycled dynamic polymers is that side reactions often alter the chemical composition and architecture of the polymer systems. Although DCvCs are commonly touted as reversible reactions without unwanted side reactions,[45] reprocessing of dynamic polymers can disrupt the integrity of the reversible motif. This problem can occur through permanent modification to polymer backbones.[107] For example, Nicolaÿ and collaborators revealed that polyisoprene vitrimers displayed significantly deteriorated mechanical performance (*e.g.*, more than 50% tensile strength loss) after more than one reprocessing cycle (30 min, 150 °C) due to oxidative degradation of the polyisoprene chains in air.[107] Although these side reactions have not caused severe issues in lab-scale polymer recycling experiments, extensive application of dynamic polymeric materials vulnerable to these unfavorable reactions may exacerbate potential long-term problems in material circulation.[89,132] There have been limited successes in overcoming such instability issues, such as incorporating antioxidants or implementing inert gas protection to avoid backbone oxidation,[107] or constructing a hydrophobic environment inside the material to resist moisture,[133] but there is much room for improvement in this aspect.

The loss of reversibility also can be caused by the gradual consumption of dynamic functional groups.[122] Examples of these undesirable reactions include hydrolysis of esters and isocyanates,[89,90,134] and dimerization/trimerization of isocyanates.[135] The design of more chemically-robust DCvCs is a strategic focal point related to polymer circularity. Poly(siloxanes) represent one of the most well-known examples of robust, chemically-, and thermally-stable dynamic polymer networks.[121] The equilibrium of siloxane exchange has been well-studied for almost 70 years [136] but was just recently applied to dynamic polymer systems.[137] The dynamic Si–O exchange can be initiated by silanolates and enables chain reconfiguration in crosslinked poly(dimethylsiloxane) (PDMS) and other siloxane-containing networks for self-healing and recycling purposes.[137–139] As one example, a siloxane-crosslinked epoxy polymer was reprocessed twice at a high temperature (220 °C) without significant change in crosslink density, suggesting sufficient thermal stability during recycling.[139] In addition to siloxanes, Si–O exchange also has played a critical role in polymers crosslinked by silyl ether linkages,[65,121,140,141] which displayed reprocessability at elevated temperatures and thermal stability against side reactions. In a study of PE-based networks crosslinked by silyl ethers, these properties were exemplified by a high degradation temperature

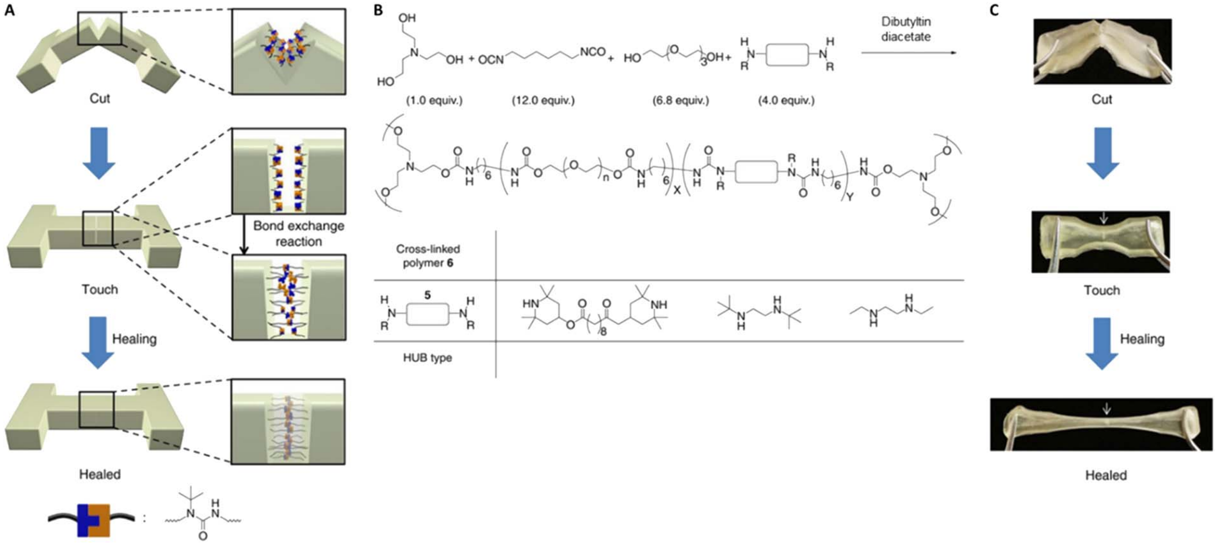


Fig. 7 Preparation and self-healing of a crosslinked poly(urethane-urea) gel with hindered urea bonds. (A) Illustration of the self-healing process *via* bond exchange. (B) Synthetic route to generate the polymer. (C) Selected snapshots during the self-healing experiment of poly(urethane-urea). The arrow indicates the cut position. Adapted from ref. 53 with permission from Springer Nature, copyright 2014.

(>400 °C), as well as nearly constant tensile strength and failure strain after three cycles of reprocessing *via* compression molding (150 °C, 400 psi, 20 min).[65]

Another robust DCvC, the D–A reaction, occurs by a [4 + 2] cycloaddition mechanism to form a cyclohexene D–A adduct which can dissociate under elevated temperatures *via* a reversible pathway.[93] The D–A reaction is a "click" reaction that exhibits several advantages for recyclable thermosets, including excellent efficiency, selectivity, and a catalyst- and byproduct-free nature. As one example, a series of small molecule-based thermosets were prepared *via* catalyst-free D–A curing[142–144] from monomers composed of multiple furans/maleimides linked by various spacer groups.[142–144] The reversibility of the D–A reaction was demonstrated through continuous reprocessing for five cycles,[143] which was enabled by the D–A adducts that partially dissociate at elevated temperatures and fully recover at 80 °C during the post-curing.[143] In another illustration, a poly(hydroxyaminoether) was formed utilizing an epoxy resin crosslinked with furfurylamine and bis(maleimide).[98] This crosslinked network was recycled through compression molding, and by virtue of the dynamic reconfiguration, exhibited similar tensile strength (30.2 MPa *vs.* 30.2 MPa) and strain-at-break (159.0% *vs.* 142.7%) as compared to the original sample.[98]

For situations in which side reactions may be unavoidable, strategies to minimize their effect through DCvC mechanism regulation have been demonstrated with the aid of catalysts. For example, the recycling of polyurethanes (PUs) and non-isocyanate polyurethanes (NIPUs) has been achieved (*e.g.*, 140 °C, 11 MPa for 2 h with a catalyst for reprocessing);[145–147] however, selectivity and side reactions related to dissociative pathways hampered reprocessing without the catalyst.[145,146] The reactions exhibited dual mechanisms involving both associative transcarbamoylation and dissociative reversible isocyanate/cyclic carbonate aminolysis.[135,146,148] To suppress undesirable pathways, new and more efficient catalytic systems that lower reaction temperatures and balance these dynamic exchange processes have been developed to improve the circularity of PUs.[135]

DCvCs with similar mechanisms to urethane transcarbamoylation such as thiourethanes, also have been investigated as crosslinks with improved control against side reactions.[99,149,150] For example, a recyclable (110 °C, 10 MPa for 15 min) poly(thiourethane-urethane) elastomer was prepared from PU prepolymers and a trifunctional isothiocyanate crosslinker.[99] A small-molecule model study revealed that the dynamic thiourethane exchange displayed a similar dual mechanism as discussed above, such that both the dissociative reversible addition and the associative thiol exchange occurred.[149] Incorporation of a small excess (10 mol%) of thiol groups promoted this duality to improve material circularity by suppressing deleterious side reactions (*e.g.*, isocyanate dimerization/trimerization) that accompany the dissociative pathway.[149]

Beyond temperature – expanding stimuli-responsiveness. In addition to a thermal stimulus in DCvC research, light is an important trigger that could enhance recyclability. One of the advantages of using photodynamic reactions is the elimination of many side reactions initiated by heat, such as photodynamic cycloaddition.[151–153] As one example, methyl 4-[2-(4-pyridyl)ethenyl]cinnamate crystals were photo-reversibly polymerized (λ > 280 nm, −10 °C) *via* [2 + 2] photo-dimerization. The resulting cinnamate-based polymer was depolymerized with shorter wavelength UV irradiation ($\lambda = 254$ nm, 2 °C) and then resynthesized under the same initial polymerization conditions.[154,155] In another case, naphthalene-functionalized PMMA was photo-crosslinked with di-triazolinedione linkers *via* visible light-driven cycloaddition (λ > 400 nm).[156] The crosslinked/decrosslinked state was readily switched on and off by a light source, resulting in the transition between rigid and pliable forms.[156] This class of dynamic reactions can occur at mild temperatures in the absence of other reagents, which effectively prevents competition with side reactions. Fine control of the wavelength enables chemical selectivity over UV- or visible light-induced side reactions, as well as additional spatial and temporal tailoring for high-end processing.[157]

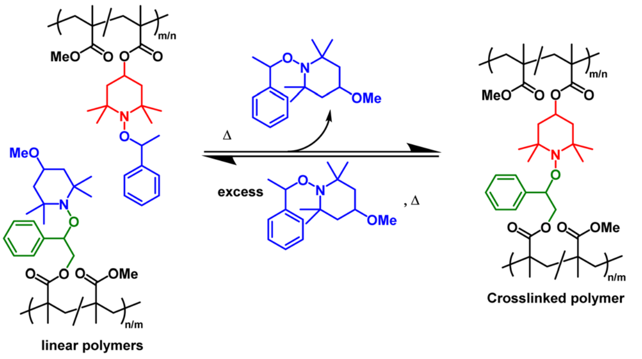
Aside from suppressing side reactions, expanding the toolbox of available stimuli beyond heat broadens potential applications and recycle/reuse scenarios. One of the most versatile DCvCs is disulfide exchange. Responding to various external stimuli, such as light,[95] pH,[158,159] redox potential,[160] ultrasound,[161] pressure,[162] and mechanical force,[163] the disulfide bond exhibits a responsive behavior that can be tailored to versatile reuse and recycle designs.[95,103,164] This broad applicability is driven by the diversity of anionic or radical mechanisms in disulfide exchange or thiol-disulfide interchanges.[158,159,165] The photo-responsiveness of disulfide bonds has been shown useful for polymer recycling *via* photo-degradation to recover monomers[166,167] and healing[166,168,169] through bond reconfiguration to repair scratches and cracks in the presence of UV light.[95,170] For example, an epoxy resin utilizing a disulfide crosslinker exhibited healing after UV irradiation for 3 min,[95] demonstrating the potential contribution of disulfide chemistry to circularity by promoting repair and reuse to extend product lifetime. Thermal treatment remains an option for reprocessing disulfide networks, similar to many other DCvCs.[103,164,172] In one study, a homogeneous film with unaltered mechanical properties could be obtained by hot-pressing (150 °C, 30 bar, 20 min) a fragmented poly(urea-urethane) elastomer containing disulfide bridges.[172]

Disulfide networks also undergo decrosslinking in solution through reduction of the disulfide linkages into thiols in the presence of small molecule thiols or phosphines (*e.g.*, 50 °C, 24 h in dimethylformamide),[171] showcasing the potential for chemical recycling.[95,166] The recycling of DCvC-crosslinked polymers *via* selective dissolution and decrosslinking under mild conditions provides a potential opportunity to simplify sorting procedures, as a complementary strategy to mechanical recycling.[57–59] After solvent-based reprocessing, the refabricated polymers from recovered monomer exhibited no loss in properties, leading to an ideal, circular polymer economy.[43] In fact, a large fraction of networks based on DCvCs, such as alkoxyamine,[173] D–A reaction,[98] transcarbamoylation,[131] and thiourethane exchange, have exhibited recyclability *via* decrosslinking or depolymerization in solution with the assistance of the corresponding DCvC compounds.[99] For example, PMMA networks crosslinked by alkoxyamine can be dissolved with an excess of small molecule alkoxyamines to yield linear polymers, and then re-crosslinked by adding more alkoxyamine-containing PMMA to shift the equilibrium back towards network formation (Scheme 1).[173] However, the separation and purification of recovered polymer components, as well as the consumption of chemical reagents, can be limiting factors for the solution-based recycling of these dynamic covalent polymers.

To overcome the aforementioned obstacles, the use of pH and common solvents in solution-based recycling has attracted increasing attention. DCvCs, such as imines,[174,175] boronic esters,[176] and boroxines,[58] are viable alternatives that don't require excess chemical consumption and related waste generation. In an example of solvolytic recyclability of imine-based dynamic covalent polymers, a DGEBA epoxy resin was cured using vanillin and *m*-xylylenediamine.[174] Thermal remolding of these imines led only to partial recovery of the original material strength (~40% loss). However, the imine hydrolysis under mildly acidic conditions (0.2 M HCl solution, $V_{H_2O}/V_{THF} = 2/8$, 25 °C, 8 h) and subsequent evaporation led to a defect-free recycled network with > 90% strength recovery.[174,177] The improved properties of the chemically-recycled polymer in comparison to mechanically-recycled materials (*e.g.*, almost unaltered tensile strength, failure strain, and Young's modulus *vs.* the original network)[175] demonstrated that dissolution of DCvC-based polymeric materials is a promising and complementary pathway to circularity for common thermosetting materials, such as epoxy resins.[174,175]

Boronic esters and boroxines also are popular DCvCs in vitrimer design because of their reversible nature at ambient temperatures and facile decrosslinking with excess alcohols.[176] For example, phenylboronic acid-terminated poly(aryl ether ketone) oligomers (PAEK) and (3-(3-carboxy-4-trifluoromethylphenoxy)-phenyl)boronic acid (CB) were used to design a recyclable PAEK-CB polymer.[58] The PAEK-CB polymer was fabricated in solution *via* dynamic crosslinking of boroxine, displaying good mechanical performance and recyclability through dissolution and depolymerization in the presence of ethanol (30 °C, 1 h). Following filtration and evaporation, 90% and 93% of the chemically-intact PAEK and CB were recovered, respectively.[58] The repolymerized PAEK-CB fabricated from recycled monomers showed nearly identical mechanical properties after five continuous cycles,[58] indicating the recyclability *via* dissolution of this boroxine-crosslinked system.

A key feature in this solvent-responsive system is the ability to selectively recycle the PAEK-CB *via* depolymerization from mixed polymers, simulating a plastics waste stream (Fig. 8).[58] This selectivity plays an important role in enabling recycling in complicated, heterogeneous, mixed plastics waste streams, reducing the effort required in separation and sorting, and ultimately, minimizing the property loss of recycled polymers caused by residual contaminants.[33] Similar selective chemical recycling of DCvC networks *via* dissolution from mixed commodity polymers has been accomplished *via* diketoenamine hydrolysis and reversible nucleophilic aromatic substitution of cyanurate.[57,59] The corresponding polymers were depolymerized and extracted in monomer form through hydrolysis (5 M H_2SO_4, 25 °C, 12 h) and base-catalyzed alcoholysis in refluxing ethanol (5 wt% K_2CO_3, 90 °C, 16 h), respectively.[57,59] Although there is still room for improvement with respect to the time required for depolymerization, these



Scheme 1 Reversible crosslinking/decrosslinking reactions between the complementary reactive alkoxyamine units (denoted in red and green) in linear polymethacrylates precursors. The reaction is tuned by the small-molecule alkoxyamine byproduct (denoted in blue) Adapted from ref. 173 with permission from Springer Nature, copyright 2013.

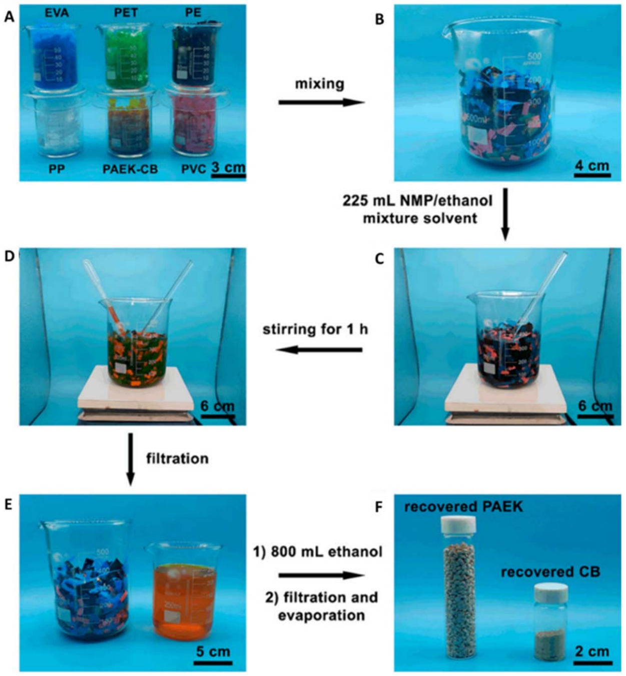


Fig. 8 Selective separation of the PAEK-CB polymer from mixed plastic waste streams. (A) PAEK-CB polymer (~8 g) and five types of commodity plastics (~42 g) were (B) combined in a beaker to generate a plastic mixture. (C) *N*-methylpyrrolidone (NMP)/ethanol was added to the plastic mixture and (D) stirred for 1 h at 30 °C. (E) The filtrate containing PAEK and CB monomers was separated from the remaining plastic solids and (F) PAEK and CB monomers were isolated from the filtrate. Adapted from ref. 58 with permission from the American Chemical Society, copyright 2022.

recycling approaches are promising due to the dissolution and subsequent refabrication of the dynamic polymers from mixed waste streams. The selective responsiveness is attractive for simplifying sorting procedures and reducing costs in waste polymer recycling protocols without impacting the recycling process of other polymer components.

There are considerably more reports on DCvC implementation in covalent networks than linear polymers (Table 1), yet a few dynamic thermoplastic polymers have been investigated in the context of solution-based recycling.[150,178,179] For instance, Lehn and collaborators employed an imine-containing diol in a linear PU to introduce DCvC into this thermoplastic polymer.[180] The polymer film was decomposed by immersion in water (50 °C for 14 h), whereby the number average molecular weight (M_n) decreased from 13 kDa to 7 kDa as a result of the dynamic hydrolysis of the imine linkages. After drying at 80 °C for 240 h, the imine linkages in the dynamic polymer (*i.e.*, dynamer) reformed, and the polymer recovered back to the original M_n.[180] A more recent study provided a general copolymerization approach towards chemically recyclable vinyl polymers through the introduction of a thionolactone cleavable comonomer.[179] After deconstruction of the thioester-containing polymers with cysteamine, the thiol-terminated fragments could be reconfigured into new polymers *via* condensation of the disulfide groups with full recovery of elastic moduli at room temperature.[179] In another example, an innovative three-component DCvC was developed to prepare linear dynamic polymers.[178] This system involved the reaction of bis-salicylaldehyde, oligo(ethylene glycol) diamines, and 2-mercaptobenzaldehyde at room temperature to produce linear polymers ($M_n \leq 20.1$ kDa).[178] The polymer dynamically exchanged the monomer units with external 2-mercaptobenzaldehydes under mild heating (70 °C).[178] Depolymerization was realized under mildly basic conditions (pH 8.0) to recover the constituent oligomers,[178] facilitating thermomechanical reprocessing.

Commodity polymer valorization

While new dynamic covalent polymeric materials offer huge potential for reprocessability and recyclability under various conditions,[49,106] it is equally important to translate these synthetic advances to existing plastics waste.[2,21] Commodity plastics include LDPE, HDPE, PP, PVC, PS, and PET,[181] and are the main contributors to the plastics accumulation problem due to an overall recycling rate below 10 wt%.[41,42]

The utilization of DCvC to transform existing commodity polymers into dynamic, recyclable polymers is a promising pathway toward polymer circularity *via* post-polymerization modification.[49,105] Although many of the commodity polymers are recyclable in principle, the downgrading of recycled materials and the unfavorable cost of reprocessing are general limitations to circularity.[23] The introduction of reversible-bond exchange *via* DCvC addresses these issues,[51] providing property enhancement and higher value to cover the cost of recycling.[41,60,61] This industrial translation is critical to enabling circularity.[105]

DCvC post-polymerization modification on PE has been successful in minimizing undesirable chain alteration during recycling.[61,105] One example involved the introduction of dioxaborolane into HDPE through reactive mixing.[61,105] A maleimide with dioxaborolane functionality was grafted onto HDPE followed by dynamic crosslinking in the presence of a bis-dioxaborolane crosslinker *via* reactive extrusion.[105] The successfully crosslinked HDPE was no longer soluble in xylene (gel content ∼31.7%) yet remained extrudable, and the tensile strength was maintained after three cycles of compression molding (150 °C, 10 min).[105] These changes in solubility and reprocessability suggested the transformation of a commodity HDPE into a recyclable vitrimer. Decrosslinking and full dissolution were achieved on the reprocessed material in the presence of excess 1,2-diol,[105] not only demonstrating the chemical recyclability of the network, but also highlighting the absence of permanent non-dynamic crosslinking after

Table 1 General advantages and considerations of common DCvCs[a]

Dynamic covalent chemistry	Advantages	Considerations
Transesterification	Tunable exchange rates	Metal salt catalysts: limited solubility, leaching, corrosion Organic base catalysts: toxicity, high cost
Alkoxyamine	Tunable *via* electronic effect	Additional virgin feedstock required for decrosslinking/re-crosslinking
Imine	Chemically recyclable	Prone to hydrolysis
Hindered urea	Tunable *via* steric hindrance	Prone to hydrolysis
Siloxane; silyl ether	High thermal stability	Lewis acid catalysts: leaching, corrosion Metal silanolate catalysts: catalyst deactivation, corrosion
Diels–Alder	Highly selective	Exchange rates predetermined by chemistry selection
(Thio)urethane	Accessibility	Prone to side reactions Organotin catalysts: toxic Rare earth metal catalysts: leaching, high cost Organic base catalysts: prone to hydrolysis
Disulfide	Responsive to various stimuli (heat, light, redox, *etc.*)	Multiple, non-selective triggers for exchange Susceptible to oxidation and side reactions
Boronic ester; boroxine	Mild reprocessing conditions	Prone to hydrolysis

[a] This table presents a list of common attributes for the specified DCvC chemistry and is not intended to be comprehensive.

reprocessing, which is a common occurrence in PE mechanical recycling.[16]

In addition to the reprocessing of modified HDPE, the vitrimer crosslinked by dioxaborolane groups displayed efficient weldability with PMMA modified with the same DCvC, without the need for an extra compatibilizing tie layer.[105] The chemical compatibility of the dioxaborolane-containing polymers improved general adhesion between PMMA/PE layers, whereas the dynamic bond exchange reinforced the welded seam through the formation of covalent bridges between the two vitrimers.[105] The dynamic interfacial adhesion presents a promising route to recycling mixed, multi-layer plastics with reduced sorting and minimal contamination from additives (*i.e.*, compatibilizers). The strategy is complementary to the selective dissolution approach above, but both methods can simplify the sorting process of mixed dynamic polymer waste streams and reduce the cost and labor of a closed-loop framework for the plastics circular economy.[182]

PP, another commodity plastic, also has been successfully valorized *via* a similar approach.[183] PP was grafted with maleic anhydride in a melt compounder and subsequently crosslinked with a tetrafunctional thiol linker in the presence of an organic base catalyst during extrusion.[183] The dynamic thioester crosslinking not only increased the tensile strength of PP, but also enabled versatile reprocessing *via* compression molding, injection molding, and fused filament fabrication 3D printing, with minimal impact on the mechanical properties (*e.g.*, tensile strength, failure strain) after several cycles, if the PP vitrimer was cooled slowly to reconstruct the crosslinks.[184]

Dynamic crosslinking of polyolefins (*e.g.*, PE, PP, ethylene/propylene copolymer rubbers) *via* grafting of maleic anhydride has become a popular approach. Followed by subsequent functionalization of the anhydride, other types of DCvC, such as the Diels–Alder reaction,[185,186] transesterification (Fig. 9A),[60,182] imine exchange,[187] and silyl ether exchange,[188] have been implemented in polyolefin vitrimers. Real post-consumer polyolefins also were utilized as feedstocks for transesterification-based vitrimers to highlight the compatibility of DCvCs with additives and contaminants, revealing the potential to upgrade real plastics waste.[60,182] Overall, polyolefin vitrimers showed comparable, or even slightly improved, strength and Young's modulus, and enhanced creep resistance induced by crosslinking *vs.* their thermoplastic precursors (Fig. 9B and C).[60]

Polyolefins remain a key target for DCvC functionalization to improve recyclability; however, other commodity polymers also exhibit enhanced circularity with post-polymerization modifications. In a recent investigation, Saito and collaborators reported that the PS block in a styrene-ethylene-butylene-styrene (SEBS) block copolymer could be functionalized directly with boronic esters through iridium-catalyzed aromatic C–H borylation, followed by dynamic crosslinking with hydroxyls on the surface of silica nanoparticles to form a composite.[189] The dynamic exchange in this crosslinked PS network led to reprocessability *via* compression molding in air; however, the tensile strength of the DCvC-containing PS gradually diminished during recycling (∼83% of original strength after three cycles) due to backbone oxidation, highlighting an area of improvement for future studies.[189] In addition to the aromatic C–H activation, another study probed the use of azidoformate with dioxaborolane moieties to functionalize PS *via* an aliphatic C–H insertion mechanism of nitrenes.[107] The functionalization was achieved *via* compression molding and reactive extrusion, suggesting the potential to implement this method at an industrial scale.[107]

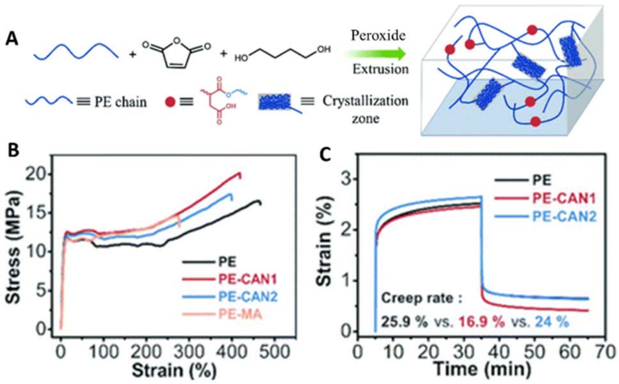


Fig. 9 Preparation and properties of maleic anhydride grafted polyethylene (PE-MA) and polyethylene covalent adaptable networks (PE CANs). (A) Scheme of preparation and structure of PE CANs. (B) Tensile testing curves of PE, PE-MA, and PE CANs. (C) Creep rates and curves at 50 °C *via* dynamic mechanical analysis (DMA) before and after modification. Adapted from ref. 60 with permission from The Royal Society of Chemistry, copyright 2021.

As the world's third-most widely produced plastic,[190] PVC suffers from the chemical instability of C–Cl bonds and a poor recycling rate as a consequence.[41] In an effort to improve the recyclability of these polymers, Yagci and collaborators reacted commercial PVC with elemental sulfur, which effectively incorporated dynamic polysulfide linkages into the network.[191] The crosslinked PVC exhibited reprocessability *via* thermal treatment up to three cycles, demonstrating the dynamic nature induced by the polysulfide linkages.[191] However, deleterious side reactions (*e.g.*, dehydrochlorination, irreversible crosslinking) on the PVC backbone progressively altered the polymer properties and eventually inhibited network reconfiguration after three cycles of reprocessing.[191] Further research is needed in this area to develop DCvCs that also stabilize the PVC backbone or do not trigger main chain deterioration.

Apart from adapting commodity polymers for enhanced recyclability, incorporating DCvCs provides alternative recycling strategies for degradable condensation polymers, such as PET and PUs.[51,147] For example, PET was reactively extruded *via* an autocatalyzed NGP transesterification in the presence of a polyol crosslinker containing an adjacent tertiary amine.[51,52,192] The resultant PET vitrimer displayed enhanced creep resistance *vs.* the neat PET and was reprocessable to yield transparent and uniform products *via* compression molding, extrusion molding, and injection molding for 3 cycles with mechanical property (*e.g.*, storage modulus) retention greater than 90%.[51,52,192] In contrast, as mentioned earlier, PET recycled through conventional reprocessing suffered from property deterioration (*e.g.*, brittleness, decreased melt viscosity) after two cycles of mechanical recycling and extrusion.[51] Similar approaches have been investigated to enhance the properties of PUs. In a recent study, reactive extrusion reprocessing of a PU foam *via* dynamic transcarbamoylation in the presence of a tin catalyst was achieved which yielded extrudate with tensile strength (50.8 MPa *vs.* 49.7 MPa) and yield point (3.6% strain *vs.* 4.8% strain), similar to those of as-synthesized PU.[147] Commodity PU foam with additives (*e.g.*, surfactants, flame retardants, stabilizers) also can be reprocessed with this approach.[147] The implementation of these continuous recycling approaches for PUs is of particular interest as they have the potential to reduce the demand for toxic precursors (*e.g.*, phosgene, isocyanate) for new PU manufacturing by recreating materials from existing, post-consumer products.[147] In comparison to conventional recycling, continuous recycling/upcycling of condensation polymers using a DCvC vitrimer framework has led to extended material lifetimes and a reduction in the (re)manufacturing costs.

In general, recycle-by-design polymers along with chemically modified commodity polymers that incorporate DCvC have been proven effective in improving the potential for circularity. Synthetic efforts have increased creep resistance, tuned equilibria, and expanded reprocessing conditions (*e.g.*, temperature, time, stimulus). However, to further optimize conditions for reprocessing/recycling, synthetic knowledge must be coupled with a comprehensive physical understanding of dynamic covalent polymeric materials.

DCvC modeling, prediction, and physical behavior

The implementation of DCvCs into polymeric materials leads to challenges in the development of reliable physical models to predict the properties of dynamic polymers, particularly crosslinked structures and vitrimers. These physical models are necessary to guide the design of recyclable dynamic polymers suitable for industrial processing and various end uses.[122] For example, engineering the characteristic relaxation time (τ_R) and tuning the Deborah number ($\mathrm{De} = \tau_R/\tau_{obs}$, in which τ_{obs} is the time of observation or processing) of dynamic polymer systems are important aspects related to (re-)processing. For dimensional stability, the dynamic polymeric materials must exhibit slow network rearrangement (*e.g.*, $\mathrm{De} \gg 1$, $\tau_R \sim 10^3\ \mathrm{s} \rightarrow \infty$ at use temperatures),[66] yet they must maintain reprocessability or recyclability at shorter time scales under appropriate stimuli for circularity. DCvC-containing polymers can possess several relaxation time- and length-scales that are integrally dependent on the specific chemistry, polymer architecture, and microphase structure of the material. Thus, the prediction of macroscopic properties from the macromolecular structures and dynamic bonding characteristics provides insight into the application and reprocessing of the polymer.

Understanding the structure–property relationships of DCvC-based polymers involves the identification of a material's thermal transitions, and in the case of vitrimer networks, the topological freezing temperature (T_v), which classic thermoplastics and thermosets do not possess.[97] The T_v is the temperature at which the dynamic covalent bond exchange becomes slower than the experimental time scale of relaxation, leading to a topologically frozen network.[97,114] Generally, the T_v is the temperature at which the melt viscosity is equal to 10^{12} Pa s, which is also associated with the liquid-to-glass transition.[97,193,194] This temperature is distinct from the glass transition temperature (T_g), which is the arresting of cooperative motion and decrease in molecular mobility. Although they are independent transitions, the T_g and T_v can be affected by similar phenomena, and both affect reprocessing conditions. For example, increasing the crosslinking density of a polylactide-based vitrimer increased both the T_g and T_v.[195] However, when a higher loading of catalyst is added to improve transesterification rates, the T_g remained generally unaffected while the T_v was lowered by 50 °C (from 235 °C to 185 °C).[114,195] The identification of the T_v in DCvC-based polymers influences the application and reprocessing of vitrimer networks, and the prediction of these transitions has gained significant interest.[196–204]

To understand the polymer relaxation modes and dynamics in dynamic covalent networks, the sticky reptation/Rouse theory provides a strong foundational basis.[196–198] Originally designed for non-covalent systems (*e.g.*, ionomers, biological macromolecules, supramolecular networks),[196,199] these theories define ‘sticky points’ as the temporary crosslinks and describe the impact on motion in the entangled/unentangled linear chains. In comparison to the unmodified reptation/Rouse model, the chain mobility in the sticky reptation/Rouse model is constrained by the temporary crosslinks when the time scale is less than the average lifetime of the crosslink. On timescales equal to or longer than the lifetime of the crosslink, stress relaxation can occur through now-permitted chain diffusion.[196] This relaxation time crossover is governed by, among other factors, the reaction potential of the dynamic covalent bond and bond strength thus highlighting the importance of an appropriately chosen chemistry for specific reprocessing conditions.[197,205] Switching from non-covalent bonding to dynamic covalent bonding leads to significant differences in the lifetime and activation energy of the bond exchange, as well as the reaction pathway. The breaking and reforming of covalent bonds are energy intensive, and therefore, have longer lifetimes than their non-covalent counterparts.[85,206] Vitrimers generally have a characteristic Arrhenius viscosity dependence with temperature,[115,207] with larger activation energies leading to longer relaxation times. Activation energies of dynamic covalent bonds range from ∼10–200 kJ mol^{-1} depending on both the dynamic bond chemistry and the polymer structure;[115] thus, several magnitudes of relaxation times are accessible. Other non-chemical factors include topological constraints, such as the number of crosslinks and chain entanglements, with entanglements between crosslinks increasing the power law dependence of viscosity on concentration in a good solvent.[197,205]

Numerous theoretical and computational studies about vitrimer networks have been conducted in recent years.[200–203] To predict dynamic covalent bond energy, molecular dynamics studies introduced an optimal bond swap energy barrier (ΔE_{sw}) with an Arrhenius temperature dependence to describe the bond exchange of the vitrimer network.[200,201,204] The impact of ΔE_{sw} was investigated and found to have an inverse relationship with extrusion rate.[201] A theoretical and computational study using the inhomogeneous sticky Rouse (IHR) model revealed that,[208–210] for crosslink exchange reactions, the viscous flow activation energy from rheology (E_a^{rh}) is usually greater than the activation energy of small molecule analogues (E_a^{sm}), which agreed well with the empirical observations.[203] This difference highlights the reprocessing time dependence on the timescale of dynamic covalent crosslinks and polymer segmental relaxation.[85,211] Neat polymers with lower T_gs will have faster relaxation times for the same dynamic covalent chemistry than a neat polymer with a higher T_g.[203] Segmental relaxation of the polymer chain is generally disregarded at temperatures well above T_g. Nonetheless, as the temperature nears T_g, Williams–Landel–Ferry[212] (WLF) and Vogel–Fulcher–Tammann[213,214] (VFT) equations describe the non-Arrhenius temperature dependence. One study used a dynamically crosslinked PS copolymer with one fast-exchanging amino-modified group and one slow-exchanging unmodified silyl ether crosslinker, which changed the topological freezing temperature by 70 °C (from 117 °C to 47 °C).[121] This design led to WLF-described dynamics at a temperature within 30 °C of the T_g, and eventually more Arrhenius-like dependence at higher temperatures.[121] In addition to the exchange mechanism and temperature dependence, another notable difference among dynamic polymers is that many of these polymers contain dynamic bonds in the backbone (*e.g.*, polyesters, imine-based dynamic polymer systems).[122] Therefore, when the dynamic crosslinks change, the backbone relaxation timescale of the polymer chains also changes. The structural variation poses new challenges to models that attempt to predict activation energies and viscous flow behavior of DCvC-based polymers.

Dissociative chemistries also can experience structural variations, thus models with exclusively associative DCvCs at crosslinking points are inadequate to describe the behavior of dissociative networks. One major difference is that dissociative dynamic networks usually experience a decrease in crosslink density at elevated temperatures. The reduced crosslinking is determined by an enthalpy change (ΔH) of the dissociative reaction.[78,215] Usually, the considerable ΔH value of the dynamic dissociative reactions, such as the Diels–Alder reaction (-157 kJ mol^{-1}),[88] supports the empirical conclusion of the temperature dependence of crosslink density. Yet, in anilinium-salt-based dynamic crosslinked networks, which undergo dissociative exchanges, the equilibrium constant (K_{eq}) has minimal temperature dependence if the ΔH value is quite small (*e.g.*, -2.8 kJ mol^{-1}).[215] As a result, the net decrosslinking is negligible over a wide temperature range, and the network exhibits the same Arrhenius viscosity dependence with temperature as vitrimers. The crosslink exchange mechanism does not necessarily influence the practical reprocessing behavior of dynamic covalent polymer networks, which suggests the design of recyclable dynamic polymers can be considered with fewer constraints. Thus, the focus can be shifted to parameters necessary for bond exchange (*e.g.*, temperature, light) and recycling convenience.[216] As a result of rational chemical design, 1,2,3-thiazolium-based poly(ionic liquid) networks displayed either an Arrhenius dependence with temperature like vitrimers or a significant decrease in crosslink density characteristic of dissociative networks, depending on the varied ΔH value of the dissociative reaction.[217] The two different rheological responses influence recycling and refabrication processes, with the depolymerizable dissociative networks favoring applications requiring local or temporary flow.[217]

The physical explanation of the diverse rheological behavior and viscous flow activation energies in dynamic polymer networks inspires more subtle adjustments to the physical properties. Kalow *et al.*[218] discovered from both theoretical prediction and experimental characterization that, in dynamically crosslinked polymer systems, acid-derived crosslinkers with a common exchange mechanism exhibited vastly different stress relaxation rates without impacting the stiffness or viscous flow activation energy. In other recent studies,[195,219] supported by both theoretical and experimental investigations, researchers modified the polymer chains with pendant functional groups to adjust the viscous flow activation energy and relaxation behavior. The content of exchangeable groups had only a minimal effect on crosslink density.[195,219] Additionally, this adjustment resulted in an improved recovery ratio of the strength and strain-at-break (>90%) after reprocessing. These insights provide innovative strategies to fine-tune specific aspects of the flow properties of dynamic polymer networks under recycling conditions.

In the discussion above, it is assumed that the DCvC groups are homogeneously dispersed throughout the polymer. However, the impact of phase separation between the dynamic crosslinks and polymer backbones should be considered when reprocessing real DCvC-containing polymers. The influence of phase behavior on dynamic exchange reactions is complicated and has various effects on polymer recycling. For example, the dioxaborolane-based HDPE vitrimer investigation discussed previously also showcased the impact of phase separation.[105] When the HDPE was functionalized by 1,2-diol instead of dioxaborolane, phase separation induced by the diol prevented vitrimerization using bis-(dioxaborolane).[105] Even in the subsequently crosslinked HDPE vitrimer, the gel fraction was lower in comparison to other HDPE vitrimers (∼32%).[104,105,220] In a follow-up study,[221] the authors revealed that the HDPE vitrimer experienced macroscopic phase separation into dioxaborolane maleimide-rich and -poor regions (Fig. 10) due to the polarity of DCvC functional groups. The phase separation, as indicated by the polymer's opaque appearance, prevented full crosslinking of the HDPE and resulted in a relatively high soluble fraction of the vitrimer.[221] Interestingly, although a low gel fraction often is undesirable for polymer networks, the non-grafted phase-separated PE chains functioned as lubricants at the processing temperature and led to shorter stress relaxation times than anticipated, which could be exploited to adjust the recycling conditions of these vitrimers.[221] This study exemplifies the complexity of modification of commodity polymers in comparison to small molecules.[105]

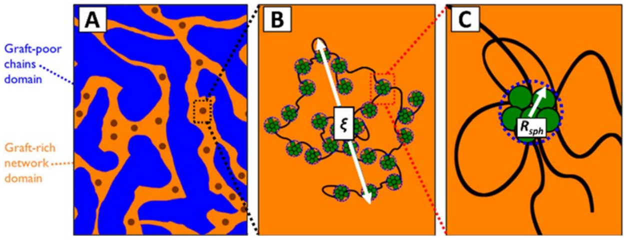


Fig. 10 Hierarchical morphology of HDPE vitrimer with crosslinker/graft-rich and -poor phases. (A) Fractals are represented by dark circles. (B) ξ is the fractal length scale. The aggregates, PE chain bridges, and PE chain loops inside are illustrated. (C) A closer look at a single graft-rich aggregate is shown within the radius R_{sph}. Associated PE chain bridges, loops, and dangling ends also are displayed. Adapted from ref. 221 with permission from the American Chemical Society, copyright 2019.

From another perspective, awareness of phase separation motivates approaches to enhance network homogeneity.[104] For example, ethylene copolymerization with comonomers containing dioxaborolane groups led to a more uniform distribution of DCvC groups on the polymer backbone, increasing the gel content to 93–99% while maintaining the tensile strength after two reprocessing cycles.[104] In addition to *de novo* copolymerization, implementing DCvC crosslinkers with good solubility and high reactivity into polyolefins could be an alternative approach to obtain homogeneous, recyclable dynamic covalent polymeric materials (*e.g.*, carbene and nitrene crosslinkers with alkyl spacers to tune the polarity and solubility in the polymer phases).[107,222]

There are opportunities to leverage heterogeneities in DCvC-containing polymers to tune mechanical properties and recycling conditions. Common post-polymerization modifications to polyolefins, such as maleic anhydride grafting,[55] can induce microphase separation. The high polarity of maleic anhydride leads to graft-rich clusters, but homogeneity is improved through the introduction of polar groups to the nonpolar polyolefin backbone.[223,224] One study compared a nonpolar polyolefin (ethylene/propylene copolymer, EPM) and a polar polymer (ethylene/vinyl acetate copolymer, EVM)[185] in which both EPM and EVM polymers were grafted with maleic anhydride, functionalized with a furan-containing imide, and then dynamically crosslinked with bis(maleimide) *via* the Diels–Alder reaction.[185] Due to the polarity difference, microphase separation occurred in the EPM-based dynamic network, but not in the EVM-based dynamic network. Consequently, after melt reprocessing, the EPM-based network exhibited almost identical mechanical performance (97% retained hardness, 7% compression gain), whereas the EVM-based network displayed moderate property loss (83% retained hardness, 27% compression loss). The authors speculated that the microphase separation in the EPM-based network resulted in polar domains with enriched furans and maleimides remaining in close vicinity, which aided the recovery of the crosslink density after the reprocessing.[185] Another study highlighted how the phase-separated clusters of associating bonds led to a high rubbery modulus and extended rubbery plateau region of the network.[225] Although this investigation used a telechelic associating polymer, similar conclusions can be extrapolated to DCvC-containing polymers and how percolation of the phase-separated domains could lead to enhanced mechanical properties and recycling.[225] Overall, aside from chemical explorations of DCvCs that have shown promise in research about enhanced circularity,[22,44,122] addressing the structure–property relationships of DCvC-based polymers is important to realize the full potential of dynamic covalent chemistries for complete polymer circularity.

Economic and environmental assessments in DCvC-based polymer recycling

While progress in synthetic and physical understanding of dynamic polymers is promising, the potential economic and environmental impact of DCvC-containing polymeric materials remains relatively unknown. Quantitative value-chain benchmarks, such as minimum selling price (MSP) and life-cycle greenhouse gas (GHG) emissions, have become increasingly important in the scale up of specific processes, particularly when evaluating circular design *vs.* conventional, linear approaches.[226] TEA and LCA are important tools for determining these quantitative values to provide additional insights about the overall effect of a new material or process on the economy or the environment. TEA typically incorporates technical and financial input parameters (*e.g.*, costs, benefits, risks) to evaluate economic performance.[227] An LCA study generally involves compiling energy and emissions information across material value chains (*e.g.*, transportation, production, consumption) to assess environmental impacts.[228] Over the last few years, several TEA and LCA studies have been published on the recycling of commercial polymers.[33,229–236] In a recent example, the LCA of an exploratory, lab-scale synthetic process for the upcycling of poly(acrylic acid) revealed a 10-fold decrease in global warming potential (kg CO_2 kg^{-1}) and cumulative energy demand (MJ kg^{-1}) when an acid-catalyzed hydrolysis approach was employed *vs.* a base-mediated route.[237] The study revealed key method optimization parameters to minimize the impact on the environment at an industrial scale, which may have been overlooked in a lab-scale study that excluded LCA.

In contrast to the cases of commercial polymers, TEA and LCA investigations of recyclable dynamic polymers are quite scarce due to the nascency of the field and the lack of industrial-scale application. For the rare instances in which TEA and LCA have been applied to recyclable dynamic polymer research,[238] the results highlighted the potential of DCvC-based materials to reduce the cost and emissions during recycling.[238] More importantly, TEA/LCA identifies the main contributors to elevated costs and emissions among the steps of the production/recycling process, motivating system optimization. For example, in practical application, only a fraction of the recycled polymer will be recovered from the waste stream and survive the recycling process. To maintain the material output of each cycle, recycled products must be supplemented with pristine polymer, increasing the expected cost and emissions of recycling dynamic polymers. Therefore, to lower the overall cost of the material, it is worthwhile to optimize the pristine material at a lab scale, using TEA/LCA to guide the synthetic pathways.

One of the few DCvC-containing materials with accompanying TEA and LCA is polydiketoenamine (PDK), which exhibits dynamic exchange of diketoenamines in the presence of an acid.[238,239] The stiffness of PDK networks was readily tuned by adjusting the formulation with commercially-available soft and hard diamine monomers,[238,240] indicating the versatility and applicability of PDKs for applications such as flexible packaging and vehicle/aircraft parts. Recycling was achieved using acid-triggered selective depolymerization and was compatible with additives and mixed plastics waste (Fig. 11),[59] showcasing PDK as a promising DCvC-based polymer for circular design.

According to TEA and LCA,[238] ideal 'circular' PDK resins showed significant decreases in MSP (\$1.5 kg^{-1} *vs.* \$45 kg^{-1}) and GHG emissions (2 kg CO_2e kg^{-1} *vs.* 86 kg CO_2e kg^{-1}) per unit mass in comparison to the primary PDK resin.[238] However, as discussed above, a fraction of the recyclate was lost during the waste recovery and recycling process.[238] Even assuming 100% PDK waste recovery, the MSP was \$9 kg^{-1} (as opposed to \$1.5 kg^{-1} for the ideal circular resin) due to material losses during the chemical recycling process that needed to be supplemented with the more expensive primary PDK.[238]

In light of the TEA/LCA observations, subsequent work[239] targeted optimization of the synthesis of primary PDK,[238] such as limiting the use of *N*,*N*′-dicyclohexylcarbodiimide and 4-(dimethylamino) pyridine in favor of more cost-effective and environmental-friendly alternatives.[239] By strategically modifying the synthetic route, the MSP and GHG emissions of primary PDK were reduced by 58% (\$45 kg^{-1} to \$19 kg^{-1}) and 66% (86 kg CO_2e kg^{-1} to 29 kg CO_2e kg^{-1}), respectively.[239]

In addition to PDKs, a dynamic polymer containing D–A adducts and hydrolyzable acetal functionalities was reported to be self-healable and closed-loop recyclable.[241] This dynamic polymer was prepared from bis(maleimide), biomass-derived 5-hydroxymethyl furfural, and pentaerythritol. The dynamic D–A reaction led to self-healing under heat treatment (30 min, 130 °C), and chemical recycling was achieved *via* acid-catalyzed hydrolysis of cyclic acetal as well as retro-Diels–Alder reaction.[241] A multi-solvent extraction method was employed to recover 95 wt% of the original polymer as monomer and D–A adducts by fractionation in different green solvents.[241] TEA indicated that the MSP of the recycled polymer (\$8.17 kg^{-1}) was

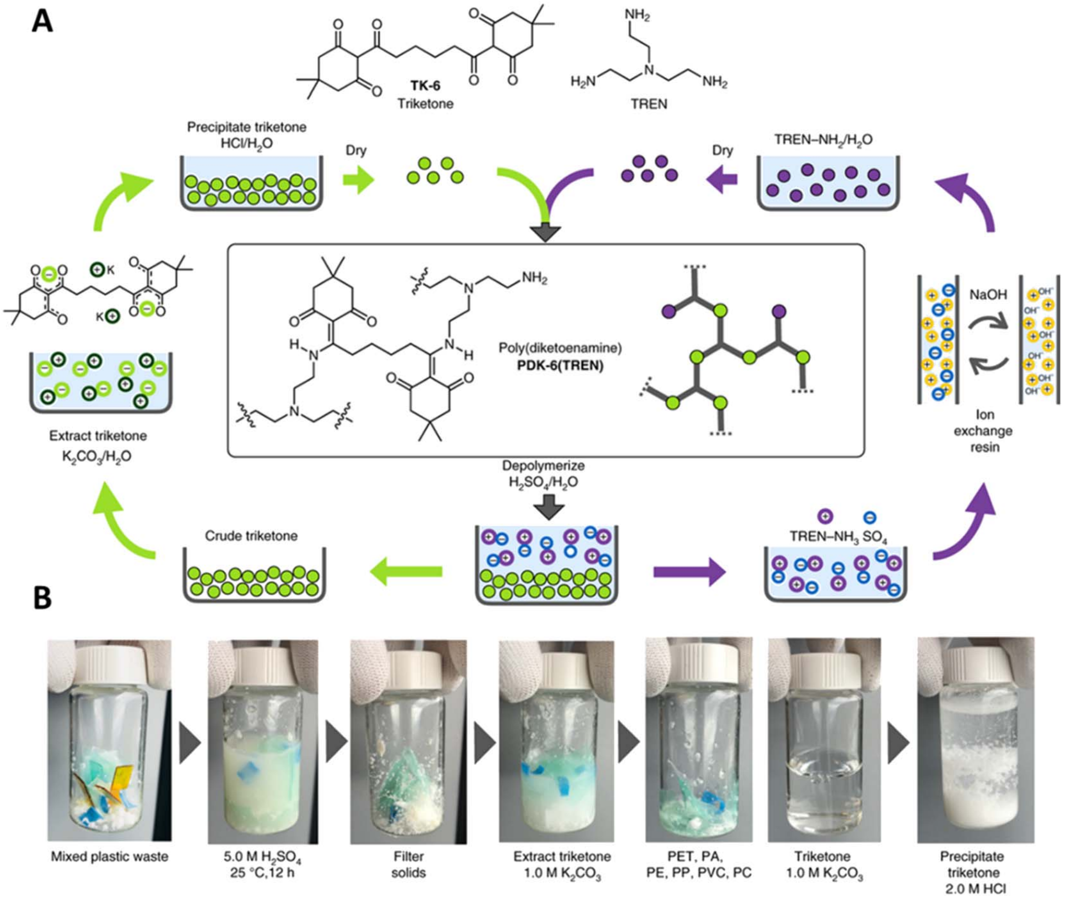


Fig. 11 The preparation and recycling of PDKs. (A) The circular design of network PDKs. The starting polyamines and ditopic triketones are recycled after hydrolyzing PDKs in a strong acid. (B) Photographs suggest the orthogonality of depolymerization and monomer recovery in the presence of PET, nylon-6,6 (PA), PE, PVC, and polycarbonate (PC). Adapted from ref. 59 with permission from Springer Nature, copyright 2019.

19.5% lower than that of the virgin polymer, emphasizing a potential benefit of dynamic polymer usage and recycling.[241]

Advances in TEA and LCA of DCvC-containing polymers are critical to inform future studies that target polymer circularity. Open-source options exist for both TEA and LCA (*e.g.*, Biorefinery Simulation and TEA Modules (BioSTEAM), openLCA, Materials Flows through Industry (MFI) tool) to aid in the preliminary design and calculation of economic and environmental impacts of newly synthesized DCvC-based polymers.[227,242,243] The results will guide method optimization during lab-scale development and identify optimal application areas for DCvC-based polymers that utilize their unique features.[239] Unfortunately, most dynamic polymers have yet to be evaluated in applied scenarios and are lacking the relevant data (*e.g.*, GHG emissions, overall energy demands, costs) to make direct comparisons with incumbent materials. Moving forward, studies that focus on expanding the available economic and emissions data to include chemicals and processes relevant to DCvC-containing polymers will be crucial. These activities will include determining specific sources for comparison (*e.g.*, solvents, feedstocks), identifying top process contributors (*e.g.*, energy, GHG emissions), and considering the value chain as a whole to evaluate the impact of waste recovery *vs.* pristine polymer production.

Beyond the calculations of MSP and GHG emissions resulting from TEA/LCA studies, a number of other environmental impacts (*e.g.*, biodegradability, microplastics formation) of DCvC-based polymers should be considered.[244] As one example, a recent investigation showed a biobased vitrimer made with soybean oil and containing boronic ester dynamic bonds had superior seawater biodegradability *vs.* a corresponding thermoset with static crosslinks.[244] The results suggested that an additional benefit of DCvC could be minimal waste accumulation,[244] yet dynamic polymers are rarely studied for their environmental compatibility, which is anticipated to be strongly impacted by different functional groups and building blocks. Because a significant fraction of plastics enters the environment, it is imperative to investigate the potential effects of DCvC-based polymeric materials on the ecosystem.

Conclusion and outlook

The global plastics waste problem necessitates interdisciplinary innovations to promote circularity in plastics production and consumption. The path forward should include the design of new, sustainable, and recyclable materials, along with the ability to tackle existing plastics waste without compromising properties that make plastics desirable (*e.g.*, high strength-to-weight ratio, durability, economic feasibility). As such, DCvC-containing polymeric materials are uniquely positioned to reduce plastics waste by enabling the recycling and reprocessing of post-consumer polymeric materials. Synthetic strategies guided by the principles of equilibrium, reaction kinetics, and stimuli-responsiveness for DCvC have produced numerous recycle-by-design strategies for new materials and post-polymerization modifications for existing commodity polymers. Physical models have been proposed to demonstrate the unique thermomechanical properties of dynamic covalent polymers that are crucial considerations in the optimization of processing and reprocessing techniques. Although currently limited by a lack of relevant data, TEA and LCA have in some cases quantified the economic and environmental impacts of recycling DCvC-based polymeric materials from a systematic perspective, guiding method optimizations towards more sustainable, cost-effective approaches.

Yet, many of these current solutions have been obtained in the vacuum of a single field (synthesis, physics, engineering, data science, environmental science, economics, *etc.*) and approached only from the laboratory scale. The realization of circularity for plastics using dynamic polymeric materials will require tight integration of all fields and close collaborations between research institutes and industry. In particular, these interdisciplinary efforts should work towards establishing an integrated feedback loop between TEA/LCA and material design. Future studies should take advantage of TEA/LCA-informed experimental approaches, such as evaluating the role of cost in catalyst selection and estimating GHG emissions associated with changes to synthetic processes. Additionally, potential end-of-life impacts should be evaluated with the engagement of environmental scientists (*e.g.*, microbiologists, ecologists). Prediction and exploration of physical properties and fine-tuning of chemical reaction behavior in DCvC-based polymers also can be enhanced through emerging artificial intelligence options, polymer-specific notations, and databases (*e.g.*, BigSMILES, CRIPT).[245–247] Aside from material-based concerns, social and behavioral challenges associated with waste plastics recovery also limit closed-loop recycling of polymer plastics waste.[17–21] Long-lasting solutions toward circularity will require not only multidisciplinary scientific advances but policy reform from industry and government, and elimination of social barriers to recycling.[17–21] With persistence on all fronts, dynamic covalent chemistries are poised to address several plastics' end-of-life challenges and accelerate the realization of closed-loop circularity in polymeric materials.

Author contributions

All authors contributed to the writing of this manuscript.

Conflicts of interest

The authors declare no competing financial interests.

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