CHEMISTRY OF MATERIALS

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Polyolefins Vitrimers: Design Principles and Applications

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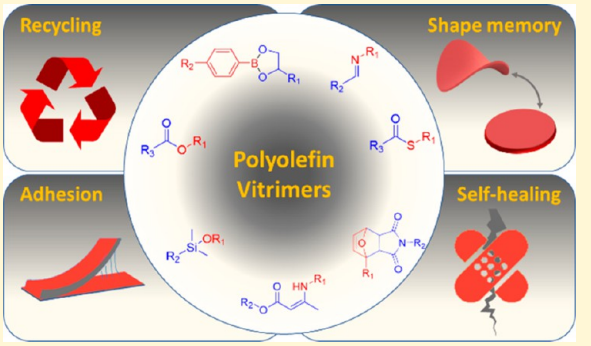
ABSTRACT: Less than 10% of plastics are recycled worldwide, among which polyolefins, which form two-thirds of all produced polymers, are the most discarded ones. This stems from the nonpolar nature of polyolefins, which limits their degradation and recycling. As such, any approach that may promote the recycling of polyolefins can significantly shift the statistics of polymer recycling toward a more sustainable future. To account for that, the vitrimer concept proposes a unique solution that not only increases the polarity of polyolefins, and as such promotes their degradation, but also expands the utility of polyolefin elastomers and compensates for the significant loss of mechanical properties upon sequential mechanical recycling in thermoplastic polyolefins. Vitrimers are polymer networks formed by reversible covalent cross-links that undergo percolation-conserving exchange reactions at high temperatures. Therefore, while they form a solid network at the service conditions, they can be reprocessed and recycled above a temperature threshold. Thanks to this, they have applications at the interface of thermoplastics and thermosets ranging from recyclable, self-healing, and adhesive materials to creep-resistant and shape-memory networks. This Review aims to classify cross-linking chemistries employed for the production of polyolefin-derived vitrimers and highlight subsequent changes in material properties and applications to promote further development of novel polyolefin vitrimers.



1. INTRODUCTION

About one hundred years ago, Staudinger separated the field of polymer science from that of small-molecule colloids by demonstrating the chemical connectivity of repeating units. Since then, advances in polymer science and technology have significantly impacted our daily lives. Although polymers have brought many sustainable solutions to human problems, such as decreasing fuel consumption through lightweight transportation, increasing food lifetime through smart packaging, and providing drinkable water through membrane technology, the problem of polymer waste accumulation has become one of today's main environmental issues.[1,2] This mainly originates from the durability of synthetic polymers and problems with separating, sorting, and recycling used polymers. On one hand, thermoset polymers, which are defined by a 3D network of interconnected chains, are not reprocessable, as reprocessing requires the selective breakage of chemical cross-links.[3] On the other hand, thermoplastic polymers undergo severe thermo-oxidative chain-breaking degradation during the traditional mechanical recycling processes, so their mechanical properties decrease significantly.[4] One of the recent advances in the field of polymer chemistry, which offers an exceptional solution to these problems, is the development of the so-called "vitrimers".[5−8] This terminology was first coined in the seminal work of Leibler et al., where plasticity was introduced in a cross-linked epoxy network by replacing chemically inert cross-links with dynamic covalent ester bonds that could undergo exchange reactions with free hydroxyl groups.[9] By allowing chemical cross-links to efficiently exchange between different positions along polymer chains, macroscopic flow could be achieved without compromising the network percolation.

Dynamic covalent bonds are classified into two main groups based on their cross-link exchange mechanism.[10−14] The first group makes use of the dissociative exchange mechanism, where chemical bonds first break and subsequently reform in another place, as illustrated in Figure 1A. A prime example of these bonds is the Diels−Alder reaction (DA), which enters an association−dissociation equilibrium above a temperature threshold. As the equilibrium constant is temperature-dependent, as shown in Figure 1A, the equilibrium shifts toward the dissociation side at high temperatures. This significantly reduces the number of cross-links and causes the loss of percolation, which results in a solid-to-liquid transformation. In contrast, in the other variant, known as the associative

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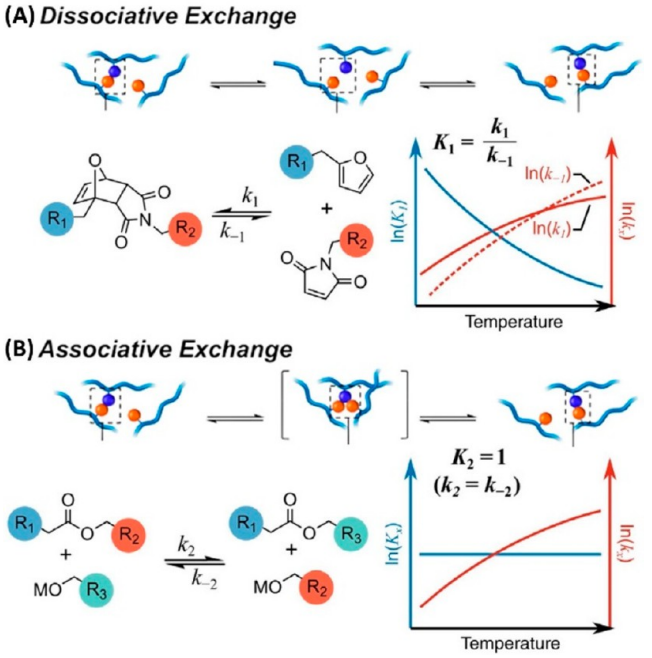

Figure 1. Schematic illustration of (A) dissociative-exchange (such as the Diels–Alder reaction) and (B) associative-exchange (such as transesterification). The equilibrium constant and the cross-linking density decrease with temperature in dissociative exchange, whereas they remain unchanged in associative exchange. Adapted with permission from refs 11 and 12. Copyright 2019 American Chemical Society and 2020 Elsevier, respectively.

exchange mechanism, a cross-link breaks only when a new covalent cross-link forms, as shown in Figure 1B. A traditional example is transesterification, where the breakage of the ester bond and the association of the free hydroxyl happen simultaneously. As both sides of the reaction include the same chemicals, the forward and reverse reaction rates are the same and the equilibrium constant is temperature-independent and equals one, as also shown in Figure 1B. The temperature increase does not change the net cross-link density but instead accelerates the shuffling reaction, which ultimately results in the flow of the material. Therefore, the key advantage of associative exchange, which makes it distinctly useful for the development of vitrimers, is the preservation of the cross-link density even at high temperatures or in the presence of a solvent. Nevertheless, many of the dissociative exchange reactions reflect equilibrium constants large enough that the cross-link density remains almost constant during the observation time at high temperatures, so they can be effectively used for the development of vitrimer-like materials.[11,15,16]

The associative character of the exchange reaction is traditionally confirmed by studying small-molecule model systems, theoretical simulations, or the Arrhenius-type relationship between temperature and viscosity in a polymer network. The latter emerges only when a small percentage of cross-links break at a certain time at high temperatures. As many reversible polymer networks based on dissociative exchange mechanisms show a similar Arrhenius relationship between viscosity and temperature, specifically the ones with a large enough equilibrium constant, many researchers have criticized using the term vitrimer only for reversible networks based on associative exchange.[11,15,16] In practice, the reprocessing feature of most reversible polymer networks does not depend on the nature of the exchange mechanism, and many dissociative mechanisms are as useful as associative ones. Therefore, the ease of synthesis and the application are the determining factors that practically outweigh the nature of the exchange mechanism.[16] Following this notion, we also cover networks based on dissociative exchange, which have been reported to provide vitrimer-like properties.

Regardless of the bond exchange mechanism, there are two main strategies for preparing vitrimers, as outlined in Figure 2.[12,13] The first strategy is based on incorporating multifunc-

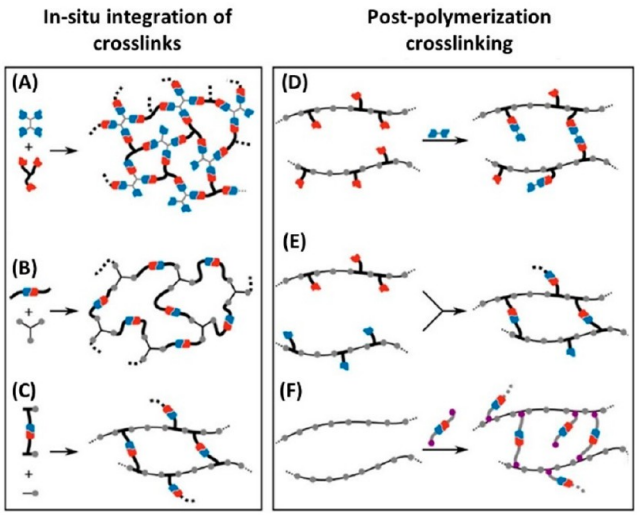

Figure 2. Strategies for preparing vitrimers. In situ integration of functional monomers in (A and B) step- and (C) chain-growth polymerization and postpolymerization cross-linking by the introduction of (D) a complementary small-molecule or (E) a polymer chain or (F) modification of the polymer chain. Adapted with permission from ref 12. Copyright 2020 Elsevier.

tional monomers that carry exchangeable functions during copolymerization, which later enable the formation of dynamic covalent bonds.[17−21] In the case of step-growth polymerization, the network can be formed along with polymerization using heterocomplementary monomers, as illustrated in Figure 2A,[22,23] or upon integrating the exchangeable bond in only one of the monomers, as shown in Figure 2B.[24,25] In the case of chain-growth polymerization, the most direct route is to introduce a bifunctional cross-linker in the copolymerization that contains the required dynamic covalent bond, as shown in Figure 2C. This method, of course, benefits from a higher degree of control over the chain structure and composition; however, it may not be compatible with the existing polymerization plants. The alternative approach is to transform the existing thermoplastic polymers into vitrimers through post-polymerization modification reactions, as outlined in the right panel in Figure 2. Despite suffering from less control over the composition and the structure, this method is particularly appealing, as does not require the modification of the existing polymerization plants. Functions required to establish the exchange reaction can already be present along the backbone or as pendant groups, as illustrated in Figure 2D. Examples include the ester or terminal alcohol functions of polyesters for vitrimers based on transesterification reactions[26,27] or the alkene bond of polydienes for vitrimers relying on the alkene metathesis reaction.[28] Alternately, heterocomplementary func-

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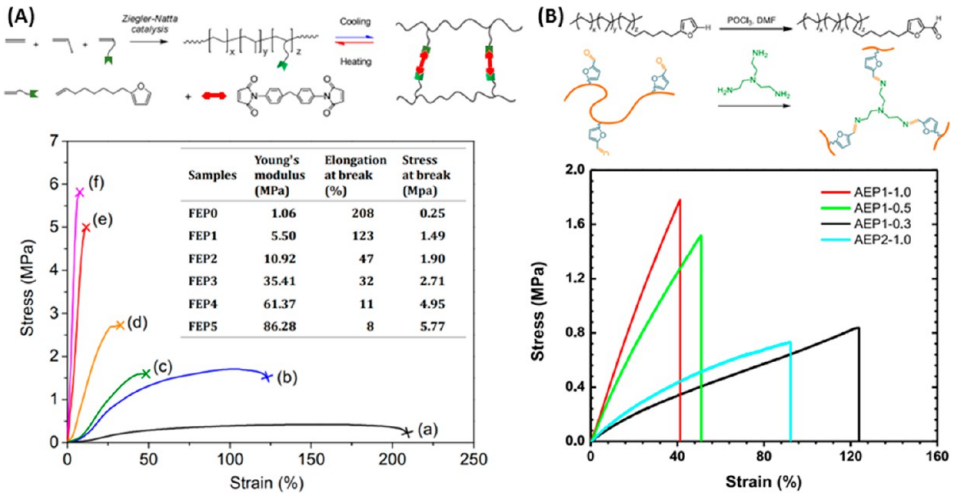

Figure 3. (A) Synthesis of a thermoreversible EPR based on DA reversible cross-links. (Top) Direct copolymerization of an ethylene-, propylene-, and furan-functionalized co-monomer, the introduction of bismaleimide, and the formation of DA cross-links. (Bottom) Stress−strain curves and the corresponding tensile parameters at the progressive formation of dynamic cross-links (samples contain varied furan and MA contents). Reproduced with permission from ref 46. Copyright 2017 Royal Society of Chemistry. (B) Formation of dynamic imine bonds between aldehyde-functionalized EPR and the triamine cross-linker. Tensile curves demonstrate the materials are progressively stiffer at larger cross-linking densities (AEP1 and AEP2 contain 4.6% and 1.4% aldehyde, respectively; numbers in the sample codes denote the amine-to-aldehyde ratio). Reproduced with permission from 48. Copyright 2021 Elsevier.

tions required to form dynamic covalent bonds can be introduced through a second polymer or a multifunctional small molecule, as illustrated in Figure 2E and F, respectively.[29,30,5,31] The chemistry required to attach cross-linkers, which depends on the reactivity of the parent polymer, should be compatible with the exchange reaction.[32,33] Moreover, with some systems, dynamic covalent bonds are activated by adding a small-molecule catalyst or adjusting the composition of the polymer.[34] With the abundance of the applicable dynamic covalent bonds, the flexibility of introduction approaches, and the choices of the network design, in-depth knowledge of the structure−property relationships of vitrimers is required to turn the desired polymer into a vitrimer. However, for a specific class of polymers, such as polyolefins, with limitations in the synthesis and post-polymerization modification reactions, a more distinct guideline can be offered. Specifically, polyolefin vitrimers are mainly based on side-chain-functionalized chains that are either made by the incorporation of functional monomers during polymerization, which turn into vitrimers via the subsequent addition of small-molecule cross-linkers, as outlined in Figure 2D, or formed by the postpolymerization functionalization with the cross-linker, as shown in Figure 2F. Very rare examples include telechelic precursors that are functionalized with the cross-linker, as described in Figure 2B.[35]

The necessity of using the vitrimer concept in the development of new olefin-based polymers is simply understood by considering that polyolefins, which constitute two-thirds of plastic products, have the most nonpolar structures and therefore the lowest potential for degradation among all polymers. The integration of exchangeable bonds not only expands the utility of polyolefin thermosets but also resolves the significant loss of mechanical properties upon sequential mechanical recycling in thermoplastic polyolefins.[1,3] To account for that, different functional groups were recently employed to achieve polyolefin vitrimers following innovative approaches including direct and indirect copolymerization reactions and postpolymerization modification. However, the sensitivity of olefin polymerization methods and the nonpolar structures of polyolefins limit the applicable chemistries and result in some specific considerations, such as microphase separation due to thermodynamic inconsistencies. Therefore, in this contribution, we provide a technical overview of the methods employed for the production of polyolefin-derived vitrimers and study the subsequent changes in material properties and their potential applications. The material basis of our survey is not limited to polyolefin homopolymers but instead to any copolymer that contains olefinic monomers. As a result, ethylene−vinyl acetate copolymers or even polybutadiene (PBd) are covered, as the latter may contain a 1,2-addition that forms an olefinic co-monomer along the chain. We hope that such a focused Review can help design new strategies to develop more olefin-based vitrimers and contribute to a more sustainable future.

2. DIRECT COPOLYMERIZATION METHODS

Direct copolymerization is an attractive method for the fabrication of dynamic networks, since the desired structure can be obtained in a single step with precisely defined molar mass, chemical composition, and chain architecture.[36] Nevertheless, specifically for polyolefin-based materials, this method is limited to special cases, as the introduction of multifunctional monomers requires a harmony between the chemistry of the exchangeable linkage, the active species in the reaction, and the polymerization conditions.

The efficiency of the catalytic system is one of the main concerns in the direct synthesis of polyolefin vitrimers. Coordination catalysts are classified into early and late transition-metal catalysts. The former are known for their extraordinary catalytic activity, high stereoselectivity, and good control over the molar mass but much lower extent of polar functional group tolerance. Despite having more tolerance toward functional monomers, the latter group has demonstrated significantly lower reaction yields.[37,38] A specific class of these catalysts introduced by Brookhart and co-workers containing Ni(II) or Pd(II) as the metal center and diimine-based ligands[39,40] can copolymerize polar monomers such acrylates with olefins in high yields; however, they inevitably form different types of short and long branches.[41−43]

Accordingly, most commercialized coordination catalysts cannot incorporate functional monomers. However, some specifically

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designed monomers are easier to incorporate, even with early transition metal catalysts. In particular, the coordination of the monomer to the active catalyst center is interfered with less if the polar group is connected to the double bond via a long alkyl spacer.[18,44] For instance, Niu and co-workers recently reported the synthesis of thermoreversibly cross-linked ethylene−propylene rubber (EPR) by first incorporating a furan-modified olefinic monomer through direct copolymerization using a traditional Ziegler−Natta catalyst, as shown in Figure 3A.[45−47] The furan group is separated from the double bond by a hexyl spacer; therefore, the fraction of polar co-monomer of the terpolymer could be increased up to 9.7 mol %. Thermoreversible cross-links were subsequently formed by the introduction of the bismaleimide cross-linker and the consequent Diels−Alder reaction with the pendant furan groups. This step was realized by the solution mixing of the functional EPR rubber, the cross-linker in hot xylene, and subsequent precipitation in methanol. Despite the dissociative exchange mechanism, these cross-links are characterized by a low coupling temperature (60−80 °C) and a high decoupling temperature (~120 °C), which make them ideal for designing thermoreversible polymer networks. Excessive cross-linking, however, significantly enhanced the elastic modulus and changed the tensile behavior from an elastic rubber to a brittle solid, as demonstrated in the lower panel of Figure 3A. Nevertheless, the reversibility of the cross-links allowed the self-healing of local cracks and reprocessability.

The same authors also used the directly copolymerized furan-functionalized EPR to form an amphiphilic co-network upon the introduction of maleimide-functionalized linear poly(ethylene glycol) (PEG) as the cross-linker.[45] A similar DA reaction between furan and maleimide was established and used to construct thermoreversible EPR−PEG co-networks. The crystallinity of PEG and the elasticity of EPR endowed the material with high strength and toughness at room temperature, while the reverse DA reaction at high temperature resulted in the complete dissolution of the network following a dissociative exchange mechanism. To address this issue, the same group transformed the pendant furan groups into aldehydes and formed dynamic imine bonds upon the introduction of a triamine cross-linker, as shown in Figure 3B.[48] Dynamic imine bonds follow an associative-exchange mechanism, which results in topology rearrangement without the loss of network percolation. The bond-exchange reaction could proceed through either the imine−imine metathesis or the imine−amine exchange process. Therefore, the reversible EPR networks became insoluble even at high temperatures. Accordingly, the cross-link density and as such the mechanical properties were simply tuned by varying the aldehyde content and the ratio of the trifunctional cross-linker, as demonstrated in the lower panel of Figure 3B.

Li and co-workers recently reported another example of the utility of direct copolymerization in the fabrication of polyolefin thermoplastic elastomer vitrimers (P-TPE).[49] This includes the synthesis of an anthracene-containing ethylene/α-olefin copolymer using the *rac*-$Et(Ind)_2ZrCl_2$ catalyst. The introduction of anthracene side groups permitted the successive grafting of N-substituted maleimide via the DA reaction. Consequently, the reversible cross-links were formed upon the introduction of a bisdioxaborolane cross-linker, as outlined in Figure 4. The reversible exchange reaction between dioxaborolane maleimide groups and bisdioxaborolane cross-linkers resulted in the formation of a dynamic network. This modification brought excellent mechanical properties and resistance to heat and solvents without compromising the elasticity and reprocessability.[49] The introduction of reversible cross-links resulted in a fivefold increase in the tensile strength while maintaining the high elongation at break and low Young modulus. An excessive increase in the cross-linking density, however, restricted the segmental mobility and resulted in the gradual reduction of the elongation at break. In the meantime, due to the reversibility of boronic ester bonds, transient cross-links dissociated at elevated temperatures, which allowed the recycling of P-TPE vitrimers without a significant loss of elastomeric properties.

Chen and co-workers have reported another direct copolymerization approach for the development of a polyethylene (PE) vitrimer

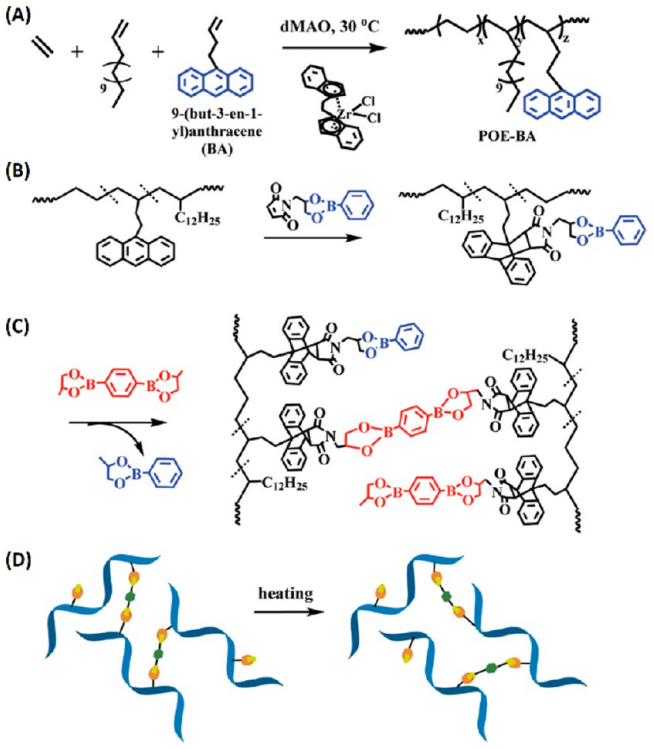

Figure 4. Olefinic vitrimers through the direct copolymerization approach. (A) Copolymerization of the anthracene-functionalized monomer. (B) Grafting of the boronic ester N-substituted maleimide through the Diels−Alder reaction. (C) Introduction of the bis-dioxaborolane cross-linker. (D) Rearrangement of the network topology by the exchange reaction. Reproduced with permission from ref 49. Copyright 2020 Royal Society of Chemistry.

based on reconfigurable alkyl boronic ester dynamic linkages.[50] For this approach, dioxaborolane-modified poly(cyclooctene) (PCOE-B) was directly synthesized via the ring-opening metathesis copolymerization of cyclooctene and methyl boronic ester-substituted cyclooctene, as outlined in Figure 5A. After hydrogenation, PCOE-B was quantitively transformed into a linear PE with dioxaborolane side groups (PE-B). To generate a PE-based vitrimer with alkyl boronic linkages (PE-AB), a 1,6-hexanediboronic ester cross-linker was prepared from 1,6-hexanediboronic acid, as also shown in Figure 5A. Upon the addition of the cross-linker to the solution of PE-B at 120 °C, gelation took place via the rapid formation of reversible bonds. Using this material, the rheological behavior of commercial PE changed significantly upon the addition of only 5 wt % PE-AB, as shown in Figure 5B. While the pristine PE showed a crossover of storage and loss moduli at frequencies as high as 2 rad s^{-1}, the blend did not show a crossover at the accessible frequency range. More importantly, the introduction of reversible bonds brought excellent reprocessing and recycling characteristics, as demonstrated in Figure 5C.

3. INDIRECT COPOLYMERIZATION METHODS

The direct copolymerization strategies are often precluded due to catalyst poisoning or uncontrolled side reactions involving catalyst components and polar co-monomers. An alternative approach would be to protect the polar group during the polymerization with an inert cap and subsequently cleave the protecting group during the workup.[36] In this way, functional groups can become equally available for the envisioned formation of reversible cross-links. Several examples of the indirect synthesis of functional polyolefins with controlled molecular structures were demonstrated by Chung and co-

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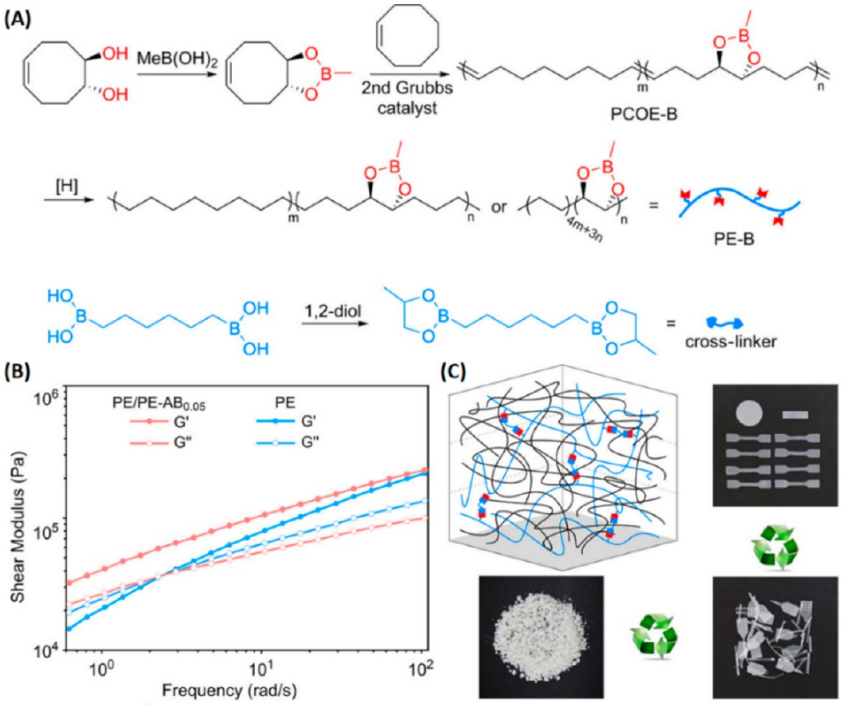

Figure 5. (A) Synthesis of the dynamic covalent network additive (DCNA): direct integration of the boronic ester-functionalized monomer, followed by hydrogenation of the backbone and the introduction of cross-linker. (B) Dynamic storage and loss moduli of PE before and after the addition of 5 wt % DNCA. (C) Reprocessing and recycling of the DNCA-modified PE. Reproduced with permission from ref 50. Copyright 2021 American Chemical Society.

workers through the reactive co-monomer approach.[51,52] The essential characteristics of the reactive co-monomer include inertness to the catalytic system, solubility in the organic reaction media, and facile conversion into the desired functional group.[53] Accordingly, organoboranes or weak benzylic protons are employed as functional groups that are inert to the coordination catalysts but can be easily converted into various functional groups, as shown in Figure 6. Moreover, organoboron functions have been demonstrated to directly form versatile types of reversible cross-links.[54−57]

Shiono and co-workers showed that unprotected arylboronic acid reacts with methylaluminoxane (MAO), which is the most common cocatalyst for homogeneous coordination polymerization catalysts.[58] This is a significant drawback for employing boronic acid-containing co-monomers in direct copolymerization. They protected the boronic acid of the co-monomer with 1,8-diaminonaphthalene (DAN)[59] and successfully copolymerized propylene using a bis(phenoxyamine) zirconium catalyst. The DAN-protected co-monomer scarcely reduced the stereospecificity of the obtained polypropylene (PP) such that the high melting temperature could be retained despite the incorporation of 3.8 mol % co-monomer. Moreover, deprotection of boronic acid was achieved along with the standard workup in acidic methanol. Boronic acid-functionalized isotactic PP showed a high Young modulus and strength following the dehydrotrimerization of the boronic acids, as outlined in Figure 7A.[60]

Another interesting example of indirect copolymerization is the work by Hillmyer and co-workers, who proposed a robust approach for the regioselective functionalization of polyolefins with alkyl substitutes such as PP and poly(1-butene) (PB) and their copolymers. This includes a rhodium-catalyzed borylation using bis(pinacolato)diboron (B_2pin_2) as the functional group,

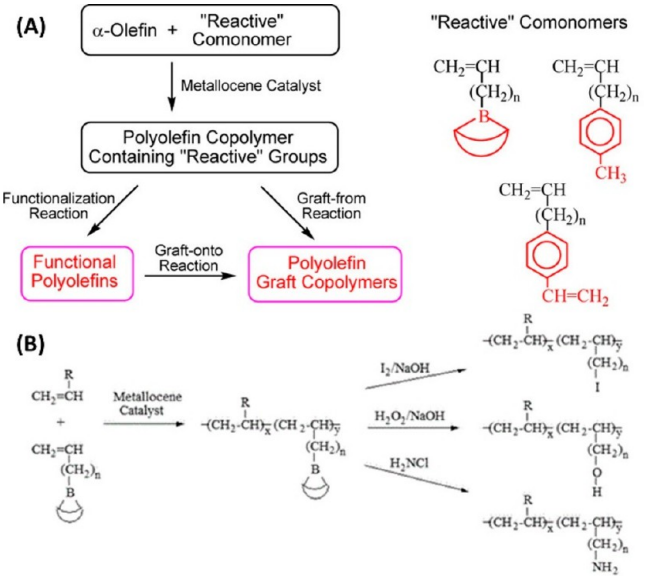

Figure 6. (A) Reactive co-monomer approach for the synthesis of functional olefin random and graft copolymers. (B) Examples of the transformation of the organoborane group into different functional groups. Reproduced with permission from ref 52. Copyright 2013 American Chemical Society.

followed by the oxidation of alkylboronate ester to generate the hydroxyl group, as shown in Figure 7B.[61] Reactions were performed in the bulk polymer substrate at temperatures between 150 and 200 °C. They oxidized the borylated polymer using H_2O_2 in THF/H_2O at basic conditions to form hydroxyl-functionalized copolymers; nevertheless, the boron-containing copolymer could be directly employed to form reversible

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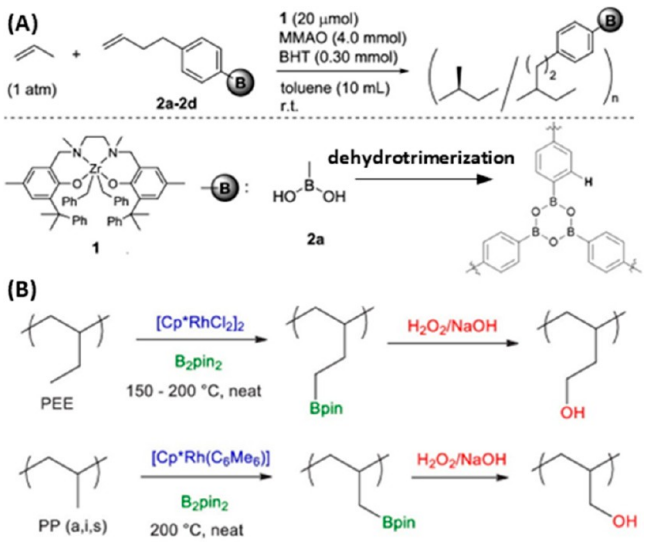


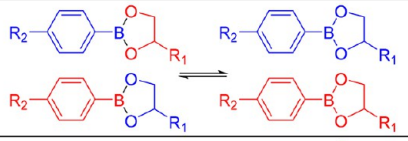
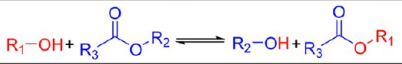
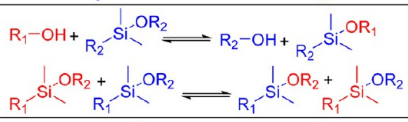
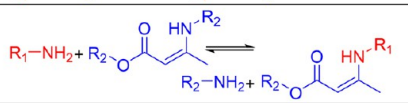
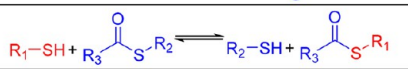
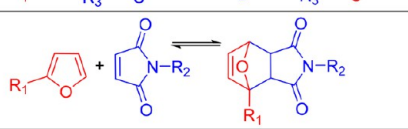
Figure 7. (A) Indirect approach for the incorporation of boronic acid containing co-monomers capable of forming reversible cross-links upon dehydrotrimerization. Reproduced with permission from ref 60. Copyright 2021 American Chemical Society. (B) Borylation of saturated polyolefins with pendant alkyl groups using rhodium catalysts. Reproduced with permission from ref 36. Copyright 2021 American Chemical Society.

networks based on boronic ester linkages. Higher degrees of functionalization were achieved at larger B_2pin_2/polymer ratios, although the catalytic efficiency dramatically decreased at elevated B_2pin_2 loadings.[62−64] A similar strategy for the indirect introduction of boryl groups into polymer chains is based on the modification of pendant carbon double bonds. For instance, Studer and co-workers introduced alkoxyamine functionalities into low-molar-mass polybutadiene (PBd) via hydroboration with catecholborane (B_2Cat_2).[65] The reaction was conducted at 0 °C in CH_2Cl_2 using $RhCl(PPh_3)_3$ as the catalyst. ^1H NMR studies showed that hydroboration occurred preferentially on pendant double bonds rather than on others inside the main backbone.

4. POST-POLYMERIZATION METHODS

As already discussed, despite the control over the chain microstructure and composition, the direct and indirect copolymerization approaches for the production of polyolefin vitrimers are challenging due to their low compatibility with the requirements of traditional coordination polymerization methods, including the low solubility of polar monomers in reaction media, their low reactivity, and most importantly catalyst poisoning.[20,21] Therefore, realizing the functionalization in a separate step after the polymerization process is the common approach to transform nonreactive polyolefins into vitrimers. The postpolymerization transformation by reactive processing is particularly appealing for industrial applications, as it does not interfere with their already optimized synthesis methods.[12] Nevertheless, this approach requires efficient grafting chemistries and dynamic bonds that are thermally and chemically compatible with reactive processing in the molten state. Moreover, the exchangeable links should be sufficiently dynamic to yield viscosities compatible with the processing conditions. Among the numerous thermoreversible cross-linking chemistries that have been explored for the synthesis of vitrimers, only select reaction strategies, as illustrated in Table 1, have been compatible enough to be employed in the production of vitrimers from commodity polyolefins. Between them, reversible DA bonds are reported to have a large enough association

Table 1. Overview of the Main Crosslinking Chemistries Utilized in the Development of Polyolefin Vitrimers

Reaction	Scheme	Mechanism[a]	Polymer backbone	Ref
Boronic ester exchange		A ND A ND A	PE PP POE PBd SBR	[5, 31, 50, 70-73] [60] [49, 74, 75] [55, 76] [77, 78]
Transesterification		A ND	PE PEVA	[32, 69, 79] [80]
Silyl ether exchange		ND ND	PE PEOH	[81] [82]
Imine exchange		A A	PBd EPR	[35, 83, 84] [48]
Vinylogous urethane exchange		A	PE	[85]
thiol–thioester exchange		A	PP	[86]
Diels-Alder reaction		D D	PBd EPR	[66] [45, 46, 67]

[a]A: Associative. D: Dissociative. ND: not discussed.

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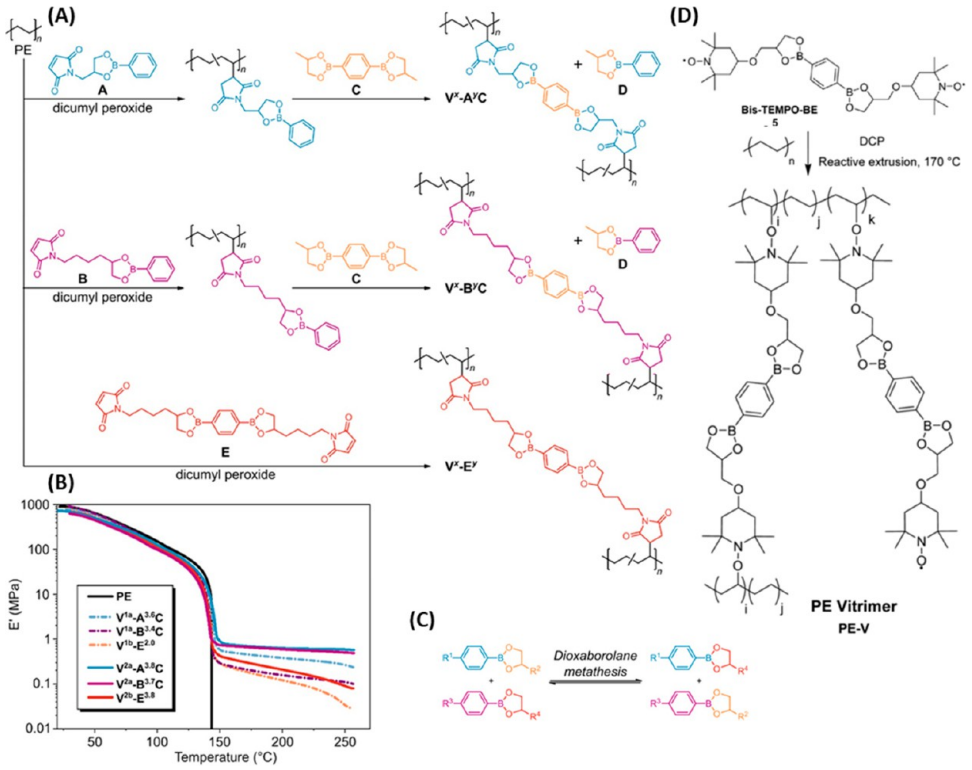

Figure 8. (A) One- (AC and BC) and two-step (E) approaches for the synthesis of PE vitrimers. (B) Dynamic mechanical analysis of PE and PE-vitrimers prepared from AC, BC, and E approaches at the frequency of 1 Hz. (C) Dioxaborolane metathesis exchange reaction. Reproduced with permission from ref 73. Copyright 2021 American Chemical Society. (D) One-step synthesis of PE-vitrimers using dinitroxide bis(dioxaborolane) cross-linkers. Reproduced with permission from ref 31. Copyright 2019 Royal Society of Chemistry.

equilibrium constant to provide stable cross-link at practical reprocessing conditions despite their dissociative exchange mechanism.[66,67] Similarly, internally catalyzed transesterification is reported to follow a dissociative exchange mechanism[68] despite being successful in providing the vitrimer-like temperature-dependence of flow properties.[69]

4.1. Boronic Ester Exchange. Dioxaborolanes are frequently used to prepare polymer vitrimers due to their high bond-dissociation energy and compatibility with a large number of chemical functions.[5,87] Therefore, they undergo catalyst-free metathesis reactions via an associative mechanism at high temperatures and tolerate chemical orthogonality.[5,87] This concept was first realized by exploiting the radical-initiated grafting of maleimides in a two-step reactive extrusion protocol, as illustrated in Figure 8A.[5] Specifically, PE was reacted with the maleimide dioxaborolane A in the presence of dicumyl peroxide (DCP) in a twin-screw microcompounder to obtain dioxaborolane-grafted PE. In parallel, bis(dioxaborolane) C was added to establish cross-links via exchange reactions. The small molecule D is liberated as a byproduct in dynamic equilibrium with cross-linkers. The resulting V-AC material exhibited a plateau modulus above the melting temperature (T_m), in sharp contrast to pristine PE, and demonstrated an enhanced creep resistance, suggesting the effective formation of the vitrimer with a percolated cross-linked network, as shown in Figure 8B.[73] This is achieved by dynamic exchange reactions following an associative mechanism at high temperatures, as illustrated in Figure 8C. Subsequent studies revealed that V-AC exhibits a complex morphology at the nano- and microscale, which has a pronounced effect on how the vitrimer flows.[71,72] The incompatibility between the PE matrix and dioxaborolane units pushed the material to form a multiphase structure with an insoluble cross-link-rich phase and a soluble cross-link-poor one. Nevertheless, the main shortcoming of using the A graft and C cross-linker to develop PE vitrimers is the release of D, as it can leach from the material over time. Although it is possible to prevent the formation of D via an additional washing step,[71] it can be problematic for scaling up the process. Nicolay and co-workers have developed a single-step alternative using the dinitroxide bis(dioxaborolane) cross-linker, as shown in Figure 8D.[31] Although small molecules were not generated in the course of cross-linking, the grafted cross-linking units suffered from poor thermal stability at conventional processing temperatures. Most recently, they utilized a new dimaleimide bis(dioxaborolane) E grafting agent, which not only allowed commercial PE to be transformed into a vitrimer in a single-step reactive extrusion without the formation of any small-molecule byproducts, as shown in Figure 8A,[73] but also exhibited better thermal stability compared to the ones obtained by dinitroxide cross-linkers.[31] Moreover, the miscibility of the grafting agent with the matrix melt was accounted for by controlling the phase separation at the nano- and microscale, which directly dictates the final thermal and mechanical properties of the material.[73]

Bao and co-workers used the two-step AC approach, as outlined in Figure 8A, to prepare a PE wax vitrimer (PEWV) based on the dioxaborolane exchange reaction, with the aim to employ it as a leakage-proof and high-energy-storing thermal interface.[70] The microphase separation that occurred between highly cross-linked chains, which formed the skeleton, and slightly cross-linked chains, which were encapsulated, avoided the leakage problem of typical PE waxes. Moreover, PEWV demonstrated a high latent heat capacity of ~121 J g^{-1}, which is about 74% of neat PE wax, due to the negligible effect of dynamic cross-linking on the crystallization of the neat wax. This negligible effect was primarily associated with the broad molar mass distribution of the parent PEW, which results in a broad distribution of lamellar thickness that may undermine the effect of introducing defects such as dynamic bonds. Moreover, the phase separation of the cross-link-rich chains has less impact on the crystallization behavior of bulk chains, and the small-angle X−ray scattering (SAXS) results confirmed that the crystalline structure was not altered after dynamic cross-linking. Meanwhile, PEWV could be plastically deformed; therefore, it tightly adhered to rigid surfaces under a slight external force at the phase-change temperature. This

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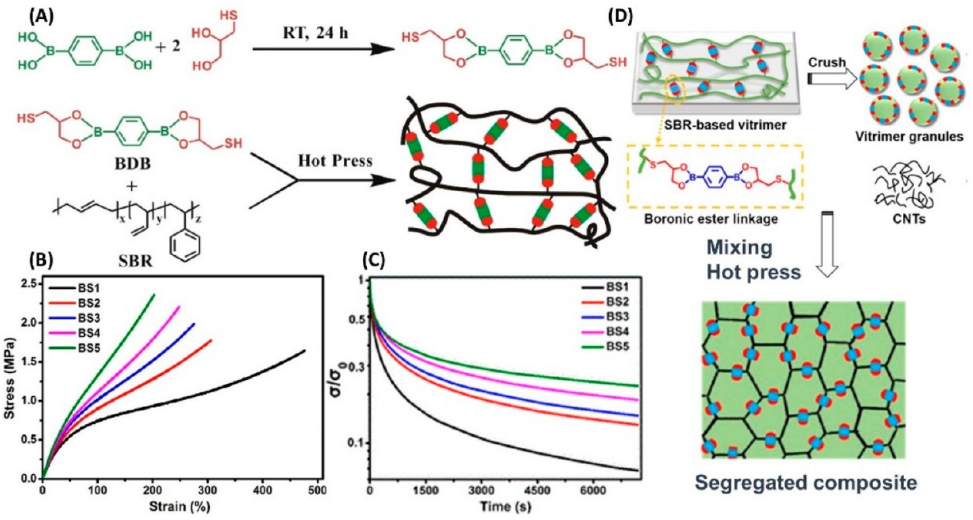

Figure 9. (A) Synthesis of the BDB cross-linker and the subsequent thiol−ene click reaction by the pendant vinyl group of SBR. (B) Tensile strengths of vitrimers at increasing fractions of BDB. (C) Stress−relaxation curves of the same samples (BSx codes represent BDB-cross-linked SBR with *x* phr BDB). Reproduced with permission from ref 77. Copyright 2018 American Chemical Society. (D) Locking CNTs at the interface of a phase-segregated SBR vitrimer. Reproduced with permission from ref 78. Copyright 2021 American Chemical Society.

allowed the filling of macro- and microscopic voids and cracks, which improved the heat transfer efficiency. The composite made of PEWV and thermal conductive fillers showed even better performance as a thermal interface material compared to commercial thermal conductive pads. Thus, PEWV with no leakage, excellent plasticity, and a high latent heat storage capacity has a great potential for application in heat storage and thermal interface management. Same authors also introduced the dioxaborolane cross-links into the commercial semicrystalline poly(ethylene-co-α-octene) or the so-called polyolefin elastomers (POE). In addition to serving as physical cross-links, the crystalline phase retarded the exchange reaction.[75] Therefore, the topology freezing temperature, T_v,[11] could be increased from −42.9 to 35.3 °C by decreasing the crystallinity upon thermal treatment.

As highlighted by Sumerlin and co-workers, the Arrhenius-type dependence of viscosity on temperature only emerges when the glass transition temperature (T_g) is far below T_v. Otherwise, for an amorphous system with a large T_g, a WLF dependence of viscosity on temperature will be observed; for the extreme case where segmental dynamics is frozen even above T_v ($T_v < T_g$), no exchange reaction may happen below T_g and the viscosity will be controlled above that by the temperature dependence of segmental dynamics rather than the exchange reaction. On top of that, for semicrystalline polyolefins, the relation between the melting temperature (T_m) and T_v becomes important. Despite the exchangeable cross-links being expected to reside only in the amorphous phase, the presence of the crystalline phase is likely to hinder the overall segmental dynamics of mobile chains in the amorphous phase.[75] Therefore, in the case the cross-links become exchangeable below the melting point ($T_v < T_m$), the net exchange rate will be suppressed; otherwise, the crystallinity should not affect the Arrhenius-type temperature dependence of viscosity.

Guo and co-workers also integrated dynamic boronic ester linkages into a network of diene-based rubbers. The network was synthesized through a one-pot thermally initiated thiol−ene "click" reaction between a novel dithiol-containing boronic ester cross-linker (BDB) and a commercially available styrene-butadiene rubber (SBR).[77] BDB was directly blended with SBR on an open two-roll mill, and the compound was subsequently compression-molded at 160 °C. During the hot press, thiol groups of BDB were coupled onto the pendant vinyl groups of SBR through a thermally initiated thiol−ene reaction, leading to the covalent cross-linking of SBR, as shown in Figure 9A. The resulting samples possessed higher mechanical strength compared to that of pristine SBR. The mechanical strength can be readily tailored by varying the boronic ester content, as reflected in the corresponding stress−strain and stress-relaxation curves shown in Figure 9B and C. Owning to the exchange of boronic ester bonds, the network topology could be shuffled, endowing the material with a good self-healing ability and malleability. The same authors recently exploited the reversibility of the network structure of boronic ester-based SBR vitrimers to lock a phase-separated structure in a polymer composite based on carbon nanotubes (CNTs).[78] As such, they formed a conductive percolated network at much lower CNT loadings compared to the classical SBR nanocomposites. Specifically, dynamic SBR vitrimers were ground into granules and mechanically mixed with CNTs to obtain CNT-coated vitrimer granules. During the subsequent hot-press molding, the transesterifications of boronic ester bonds promoted the adhesion of CNT-coated granules through molecular bonding, as illustrated in Figure 9D. In parallel, the high viscosity of the vitrimer melt forced CNTs to selectively localize at the interface. As such, coherent phase-separated composites with an ultralow percolation threshold, good flexibility, and high healing capacity were obtained.

In a similar way, Li and co-workers introduced boronic ester bonds in ethylene/1-octene POEs. Specifically, they used 5-vinyl 2-norbornene (VNB) as the third co-monomer in the copolymerization to incorporate double bonds for subsequent grafting via a thermal- or photoinitiated thiol−ene click reaction.[74] The resulting functionalized POEs were further cross-linked by bis-dioxaborolane via melt extrusion to form boronic ester-cross-linked POEs, as shown in Figure 10A. Although the reversible cross-links decreased the crystallinity, the elastic modulus and overall toughness increased. By melting the crystalline regions and enabling exchange reactions of boronic ester bonds and free hydroxyl groups, vitrimers were able to be reprocessed at high temperatures. Similarly, Bai and co-workers introduced dynamic imine bonds beside N-coordinated boroxine groups in PBd to form reversible networks.[83] First, the 2-aminoethanethiol was grafted on the pendant double bonds of the PBd rubber through a thiol−ene click reaction. The success of the grafting reaction was confirmed by DSC, which demonstrated a more than 20 °C increase in T_g upon 6% grafting. Then, amine-grafted PBd was reacted with the aldehyde group of a phenylboronic acid to form imine bonds, as shown in Figure 10B. The variation of the infrared spectra demonstrated the high reaction efficiency between the amino group and the aldehyde group. The subsequent dehydrotrimerization of boronic acid groups formed a dual-dynamic covalently cross-linked network at room temperature. The obtained flow activation energies were lower than those obtained for the single imine and the solely N-

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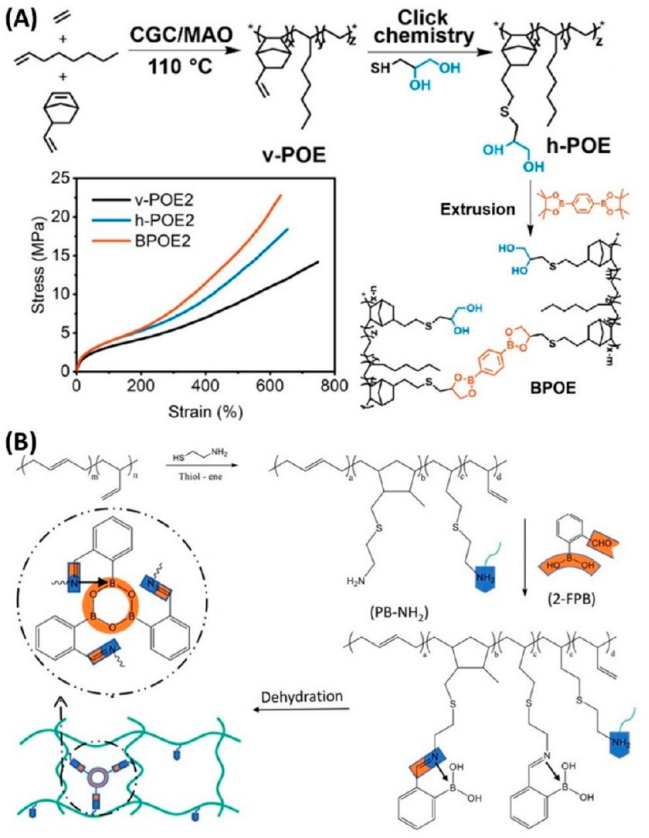

Figure 10. (A) Synthesis of a POE terpolymer and subsequent introduction of reversible cross-links by grafting diol pendants via the thiol−ene reaction and subsequent melt-mixing with bis-dioxaborolane; the corresponding tensile profiles demonstrate the improved mechanical properties. Reproduced with permission from ref 74. Copyright 2021 American Chemical Society. (B) Synthesis of PBd vitrimers based on dynamic imine bonds besides N-coordinated boroxine cross-links. Reproduced with permission from ref 83. Copyright 2020 American Chemical Society.

coordinated boroxine. Since the formation of a N−B coordination bond can stabilize the ring structure, reduce the acidity of phenylboronic acid, and accelerate the dehydration process at room temperature, the N-coordinated boroxine could endow the polymer with high strength and recyclability under milder conditions compared to simple boronic ester cross-links.

Dioxaborolane cross-links are characterized as highly dynamic associative bonds with low activation energies in the range of 40−80 kJ mol^{-1};[88] therefore, they may not be the best candidates for designing elastomers with good thermomechanical properties.[5] Specifically, if the vitrimer should only be malleable at high temperatures, then dynamic covalent bonds with higher activation energies are preferred. The ideal exchange reaction should have a high activation energy or high topological freezing transition temperatures, since dynamic links should behave like static cross-links at the service temperature to provide improved thermomechanical properties and only dissociate at high processing temperatures. Moreover, the efficiency of the exchange reaction among boronic esters strongly depends on the nature of the polymer network that encompasses these bonds. Dissociation happens faster or at lower temperatures in hydrophilic environments, while it can be hindered by the crystallinity of network chains in hydrophobic surroundings.[5,89] As such, it is necessary to account for the effect of crystalline hard phases of thermoplastic elastomers on boronic ester bond exchange and, reversely, the effect of dioxaborolane cross-links on the properties of thermoplastic elastomers with crystalline phases as physical cross-links.

4.2. Transesterification. Vitrimers based on dynamic transesterification between free hydroxyl groups and ester bonds have been widely studied and are the most frequently used class of vitrimers due to the widely available raw materials[90] and broad range of bond strengths, as characterized by the activation energy ranging between 60 and 150 kJ mol^{-1}.[88] For flexible polymers like PE, exchange reactions should effectively freeze the network topology at room temperature and be fast enough at elevated temperatures to allow the use of thermoplastic processing.[91] This is realized in transesterification by the straightforward control of the exchange kinetics via the application of external catalysts. Indeed, by changing the amount and the nature of the catalyst, the activation energy and T_v can be tuned with minimal perturbation of the material properties.[10,12] Terentjev and co-workers employed a reactive extrusion process to impart dynamic covalent bonds into the originally inert C−C backbone.[32] In this way, PP and PE retrieved from recycling were converted into permanently cross-linked networks that showed rubber-like properties above the melting temperature despite the dynamic bond exchange. Thermoplastic polyolefins were first functionalized with maleic anhydride (MA) under reactive extrusion. Subsequently, varying amounts of a diepoxy cross-linker and 1 wt % of the transesterification catalyst, $Zn(acac)_2$, were introduced at 180 °C, as shown in Figure 11A. Exchange reactions were established between the pendant hydroxyls and the added epoxy cross-linker, as illustrated in Figure 11B. Accordingly, the crystallization degree and the melting temperature were lower upon functionalization, but these vitrimers demonstrated good reprocessability and shape-memory properties. Similarly, Yang and co-workers reported a simple approach for preparing a HDPE vitrimer with a triple shape-memory effect.[79] By melt-grafting an epoxy monomer, namely, glycidyl methacrylate, epoxy groups were incorporated onto HDPE chains and served as active cross-linking sites. Covalent cross-links were formed by introducing either hydroxy-terminated polytetrahydrofuran (PTHF) or polycaprolactam (PCL), as shown in Figure 11C. Therefore, the hydroxyl−ester transesterification reaction was enabled by the carbonyl group of the functional monomer during the postprocessing step, as shown in Figure 11D. A traditional transesterification catalyst triazabicyclo[4.4.0]dec-5-ene (TBD) was selected to promote the reaction between hydroxyl and epoxy groups while simultaneously serving as a transesterification catalyst during reprocessing.

Zhu and co-workers similarly used TBD as the external catalyst to prepare reversible shape-memory polymers by integrating dynamic covalent bonds into semicrystalline poly(ethylene-co-vinyl acetate) (PEVA).[80] The abundant ester groups of PEVA were considered potential reactive sites to create reversible covalent cross-links in the presence of the transesterification catalyst. The reversible cross-links were simply provided by melt-mixing in the presence of DCP. The cross-linking mechanism of PEVA in the presence of peroxide initiators is well-established. As shown in Figure 11E, the decomposed peroxide initiator abstracts hydrogens, either from the pendant methyl group of VA monomers or from their tertiary carbons on the backbone. The coupling of these radicals provides three types of cross-links, two of which contain ester linkages and become reversible at high temperatures in the presence of TBD and the other of which is permanent. As such, the material demonstrated good thermal plasticity and nonflowing behavior above the melting temperatures.

Although transesterification-based vitrimers can show good processability, their long-term stability can be an issue due to the catalyst aging or leaching and the irreversible hydrolysis of ester bonds. To account for that, Du Prez and co-workers developed a phthalate monoester transesterification triggered by the internal catalysis of the free carboxylic acid via a dissociative mechanism without need to use an external catalyst.[68] Heuts et al. further demonstrated that the network formation is more effective and sustainable by replacing carboxylic acid with sulfonic acid neighboring groups.[92] While carboxylic acid neighboring groups inactivate over time via the formation of diesters, replacing them with sulfonic acid not only accelerates the exchange reaction but also avoids esterification. Zhu and co-workers proved that aliphatic anhydride monoesters can also carry out this dynamic transesterification.[93]

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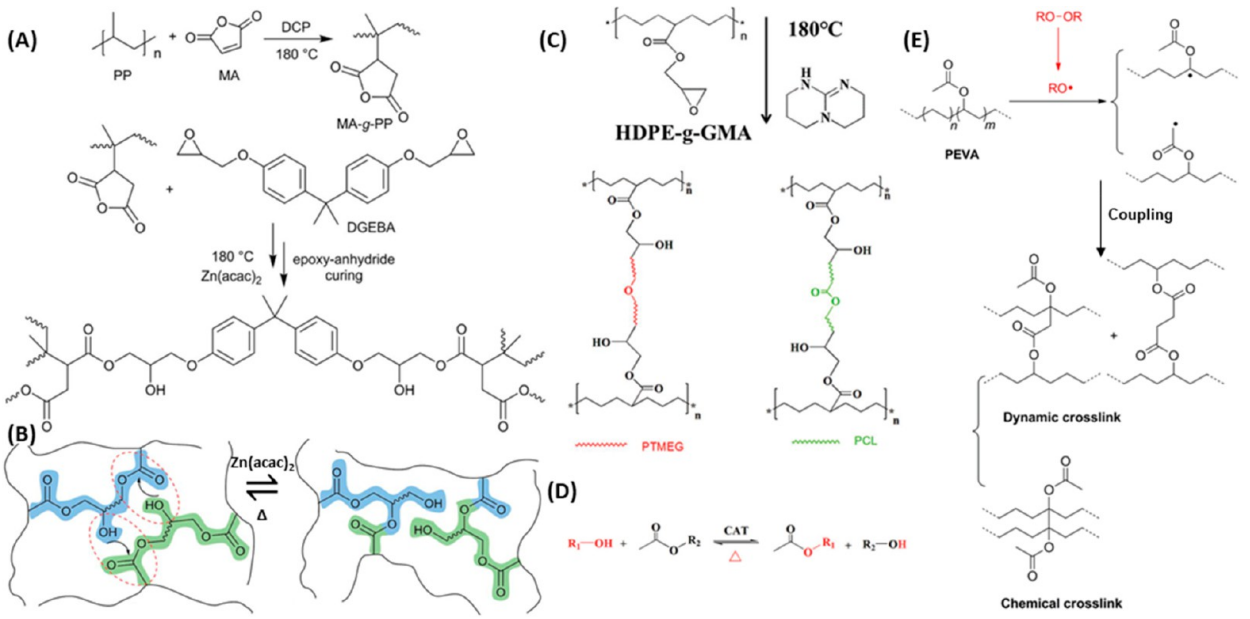

Figure 11. (A) Synthesis of the MA-g-PP copolymer and subsequent introduction of the diepoxy cross-linker. (B) Externally catalyzed thermoreversible associative bond exchange via transesterification. Reproduced with permission from ref 32. Copyright 2020 Royal Society of Chemistry. (C) Synthesis of the graft GMA-g-HDPE copolymer and the subsequent introduction of polyether and polyester cross-linkers. (D) Externally catalyzed transesterification reaction. Reproduced with permission from ref 79. Copyright 2019 Wiley. (E) Formation of reversible cross-links in PEVA by simple melt-mixing of DCP. Reproduced with permission from ref 80. Copyright 2018 American Chemical Society.

Compared to traditional transesterification that requires external catalysts, internally catalyzed anhydride monoester transesterification is more sustainable. Besides, this reaction is easier to implement in the development of polyolefin vitrimers, since radical grafting of polyolefins with MA is the most widely used method for polyolefin functionalization.[94] Besides, plenty of aliphatic diols, which are needed as the cross-linker, are commercially available. Recently, Zhu and co-workers reported the upcycling of postconsumer polyolefin products to vitrimers based on internally catalyzed anhydride monoester transesterification via an efficient large-scale and one-pot method, as shown in Figure 12A.[69] Vitrimers were produced by combining, grafting, and cross-linking postconsumer LDPE plastic bags with MA in the presence of a biobased cross-linker butanediol (BDO) and a free-radical initiator (DCP) in a twin-screw extruder. The obtained material demonstrated a plateau modulus above the melting temperature in small-amplitude oscillatory shear measurements and a delayed relaxation process in the stress-relaxation test compared to the pristine PE, as shown in Figure 12B and C.

In summary, vitrimers with reversible ester or ether cross-links, and especially epoxy-based ones, profit from the availability of monomers and the ease of synthesis, making them readily applicable on industrial scales. However, their reprocessing is only feasible at large catalyst loadings and high temperatures. Moreover, catalyst insolubility and consequent migration becomes an issue, especially when rigid monomers are used to obtain high-T_g materials.[10] To account for these shortcomings, the exploration of more dynamic catalyst-free esterification or etherification reactions will be very helpful.

4.3. Silyl Ether Exchange. Silyl ethers are reported as advantageous dynamic covalent bonds for designing vitrimers due to their facile accessibility and general applicability on top of their high chemical inertness and thermal stability,[95] as characterized by the activation energy ranging from 80 to 180 kJ mol^{-1}.[88] They can be easily introduced after polymerization by the silylation of free hydroxyl,[96] methoxy,[97] and acetate[98] or by simple copolymerization with a silyl ether-functionalized monomer.[52] Dalcanale and co-workers reported the use of reactive extrusion for the dynamic cross-linking of functional PE bearing pendant hydroxyl groups in the presence of the commercially available *N*,*N*′-Bis[3-(trimethoxysilyl)-propyl] ethylenediamine (TMSPEDA) cross-linker.[81] The fast and efficient method allowed the simple production of PE vitrimers in the

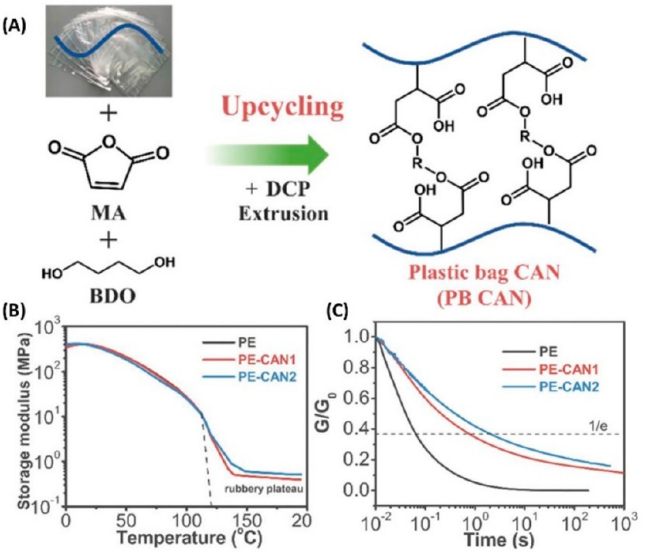

Figure 12. (A) Upcycling of LDPE films using internally catalyzed anhydride monoester transesterification. (B) Dynamic storage modulus as a function of temperature (CAN2 has higher cross-linking density compared to CAN1). (C) Stress−relaxation curves of the same samples. Reproduced with permission from ref 69. Copyright 2021 Royal Society of Chemistry.

absence of solvent. This makes the process environmentally friendly and easy to upscale. An ethylene copolymer with hydroxyethyl methacrylate (HEMA) was used as the polymer backbone to introduce silyl ether cross-links, as described in Figure 13A. The dynamic cross-linking transformed thermoplastic PE into an elastic solid and greatly improved the melting strength. The dynamic storage moduli of the pristine copolymer demonstrated terminal flow behavior, which was transformed into a steady plateau modulus for the entire accessible frequency range. Nevertheless, these bonds can be reversed upon silyl ether−hydroxyl exchange, as shown in Figure

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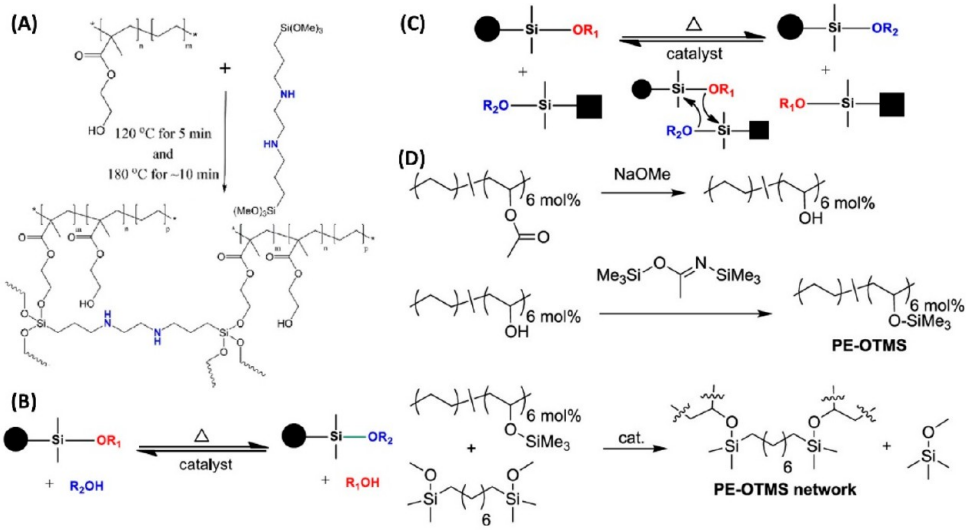

Figure 13. (A) Synthesis of dynamic covalent networks based on the silyl ether−hydroxyl exchange reaction. Reproduced with permission from ref 81. Copyright 2020 Elsevier. (B) Silyl ether−hydroxyl exchange reaction. (C) Silyl ether metathesis reaction. (D) Synthesis of dynamic covalent networks based on silyl ether metathesis, including the hydrolysis of PEVA, the silylation of hydroxyls, and the introduction of a bis-silyl ether cross-linker. Reproduced with permission from ref 82. Copyright 2019 American Chemical Society.

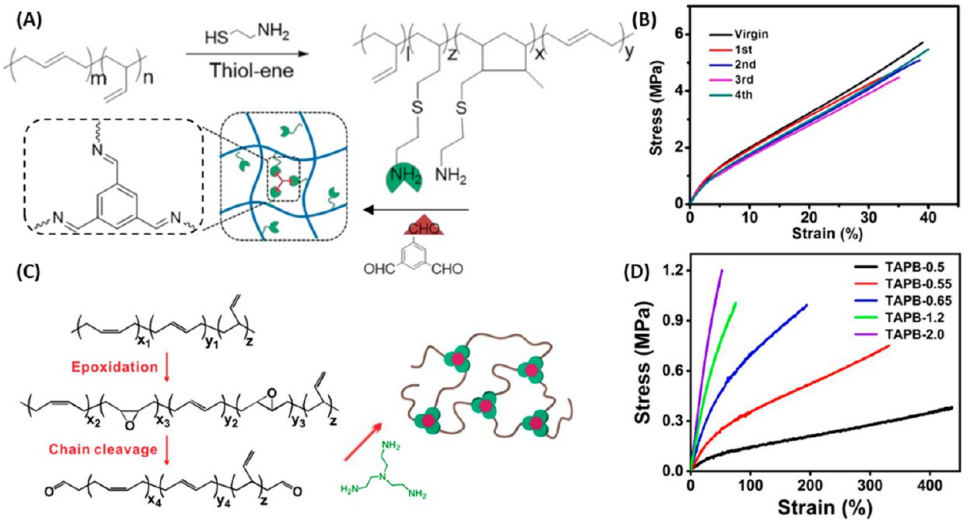

Figure 14. (A) Synthesis of vitrimers based on dynamic imine bonds through amine-group grafting using trifunctional aldehyde cross-linkers. (B) Corresponding tensile profiles demonstrate the efficient recovery of the mechanical properties after several reprocessing cycles. Reproduced with permission from ref 84. Copyright 2017 Wiley. (C) Synthesis of imine bond-based vitrimers using aldehyde-terminated PBd and trifunctional amine cross-linkers. (D) Corresponding tensile profiles reveal the consistent increase of mechanical properties with the cross-linking density (TAPB*x* represents TAA cross-linked APB-*x*, with *x* being the ratio of mCPBA to butadiene). Reproduced with permission from ref 35. Copyright 2020 Royal Society of Chemistry.

13B, which provides reprocessability. These bonds are also susceptible to hydrolysis; however, the hydrophobic nature of the PE backbone limits swelling and water uptake and as such protects reversible cross-links from hydrolysis. This is of great importance for industrial applications such as water pipes and wire coating.

One of the major limitations of such silyl ether exchange vitrimers is the necessity of having free hydroxyls on the polymer chain.[95] The presence of such hydroxyl groups not only causes side reactions such as dehydration and oxidation at elevated temperatures but also promotes possible degradative reactions.[99] This would undermine the utility of vitrimers in multiple cycles of reprocessing or recycling at elevated temperatures. To account for that, Guan and co-workers introduced bissilyl ethers as dynamic cross-linkers to design different vitrimers. First, they reported on the direct cross-linking of polystyrene functionalized with pendant hydroxyl groups using a commercially available silyl ether cross-linker.[95] More recently, direct silyl ether metathesis was employed to generate polyethylene-co-vinyl alcohol (PEOH) vitrimers with exceptional thermal stability.[82] They reported that in a small-molecule model system silyl ether motifs directly exchange under anhydrous conditions and the catalysis of external Brønsted or Lewis acids, as illustrated in Figure 13C. To demonstrate its utility in polymeric systems, they produced PEOH by the hydrolysis of PEVA and silylated hydroxyl groups with trimethylsilyl (TMS), followed by cross-linking with bissilyl ether cross-linkers, as shown in Figure 13D. The obtained thermoset material exhibited exceptional thermal stability along with malleability and reprocessability at elevated temperatures.

4.4. Imine Exchange. The imine bond, which is formed by a condensation reaction between an aldehyde and an amine, is another attractive dynamic covalent bond for the production of polyolefin vitrimers. The associative bond exchange can proceed either through imine condensation/hydrolysis, imine−amine exchange, or imine−

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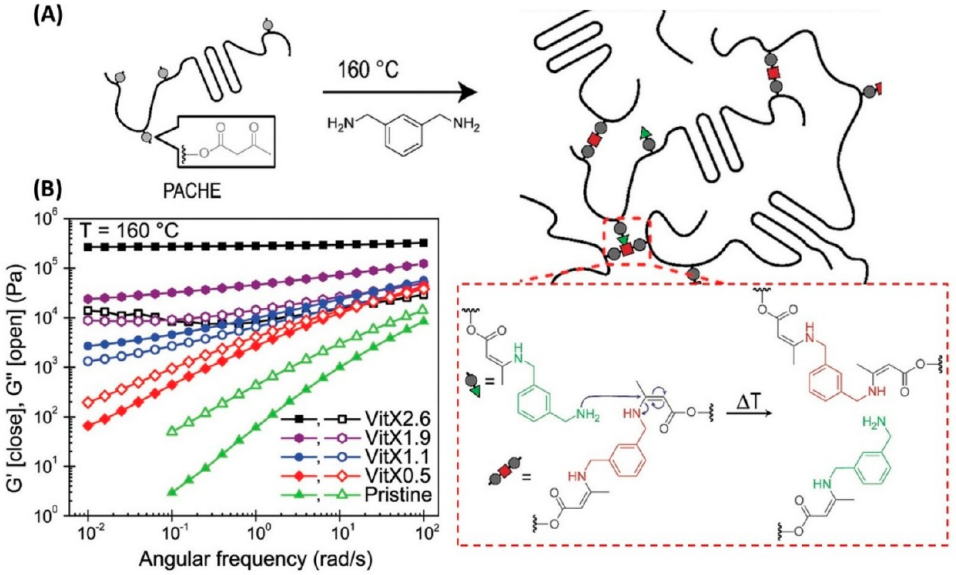

Figure 15. (A) Synthesis of LDPE vitrimers using vinylogous urethane bonds and the corresponding exchange reaction. (B) Dynamic moduli at progressively increasing fractions of cross-linkers (the numbers in the sample codes denotes the number of links per chain). Reproduced with permission from ref 85. Copyright 2019 Royal Society of Chemistry.

imine metathesis.[100] This dynamic bond provides the combination of solvent resistance and catalyst-free self-healing and recycling.[101−106] Therefore, it has been employed as a powerful synthetic tool in the design of vitrimer networks.[10,35,76,100,104,107] Accordingly, Xu and co-workers have reported the integration of pendant amine groups in PBd using a thiol−ene reaction between the vinylic double bonds and cysteamine following a radical addition mechanism.[84] PBd vitrimers with various amounts of cross-links were subsequently formed by the solution mixing of the amine-functionalized PBd and the desired amount of benezene-1,3,5-tricarbaldehyde as the trifunctional cross-linker, as demonstrated in Figure 14A. The temperature-induced imine exchange reaction enabled the recycling of cross-linked elastomers, and their mechanical properties stayed almost unchanged after several cycles, as shown in Figure 14B.

Following the same concept, Guo and co-workers prepared telechelic aldehyde-functionalized linear PBd precursors by the epoxidation of double bonds on the backbone, followed by cleavage using an equimolar amount of methyl bromo perbenzoic acid (mCPBA).[35] Linear PBd precursors subsequently formed a percolated network through the formation of imine linkages with the tris(2-aminoethyl)amine as the trifunctional cross-linker, as shown in Figure 14C. The modulus and ultimate strength of the imine bond cross-linked networks consistently increased as the molar mass of the linear precursor decreased. Interestingly, networks with a higher cross-linking density or shorter network strands showed slower relaxation times but lower rearrangement activation energies. On one hand, the slower relaxation rate of denser networks was associated with the necessity of having more imine exchange reactions to fulfill the effective network topology rearrangement. On the other hand, the corresponding lower activation energy was attributed to the abundance of imine bonds and their accessibility for the exchange reaction. Nevertheless, all samples were malleable and could recover most of their original mechanical properties after recycling, as demonstrated in Figure 14D. Moreover, chemical recycling could be performed by dissociating imine cross-links using a monofunctional amine, such *n*-butylamine, through an identical imine exchange reaction.

4.5. Other Dynamic Covalent Bonds. There is a great demand for new reaction strategies, which may enable the controlled and homogeneous cross-linking of polyolefins and as such engineering their reprocessing and recycling. The vinylogous urethane (VU) bond is one of the attractive tools that provides catalyst-free, fast, and tunable exchange of cross-links. The relatively low activation energy of 30−80 kJ mol^{-1},[88] is higher than those of traditional physical interactions such as individual hydrogen bonds[108−110] yet much lower than that of an irreversible C−C bond.[34,111] Du Prez and co-workers formed vinylogous urethane bonds by reacting acetoacetate with primary amines. The exchange reaction occurs in the presence of an excess amount of amine groups.[111] Following this concept, Dalcanale and co-workers reported a practical one-step approach for the synthesis of LDPE vitrimers via reactive extrusion using the poly(ethylene-co-2-[methacryloyloxy]ethyl acectoacate-co-2-hydroxyethyl methacrylate) terpolymer (PACHE), which was synthesized by the catalyst-free high-pressure copolymerization of ethylene and 2-(methacryloyloxy)ethyl acetoacetate (MEA) as the backbone and slight excess of commercially available *m*-xylylenediamine (XYDIA) as the cross-linker.[85] This resulted in the formation of VU cross-links in the melt, as described in Figure 15A.[85] Beyond a critical number of network cross-links, the stress-relaxation was mainly controlled by the VU exchange reaction. Reprocessability of at least four times was demonstrated by remolding, and the subsequent evaluation of the tensile strength revealed minimal degradation. Upon increasing the fraction of VU cross-links, the obtained vitrimers showed a progressive deviation from the terminal flow behavior of the pristine polymer, as shown in Figure 15B. The dynamic moduli obtained at 160 °C for samples with more than 2% cross-links resembled an elastic network with no sign of relaxation.

Terentjev and co-workers described another two-step reactive extrusion strategy for the preparation of thermoplastic polyolefins (TPOs) based on PP, which was dynamically cross-linked by the thiol−thioester bond exchange.[86] Thioester exchange offers different properties and potentials compared to the standard transesterification reaction. It is a robust and fast click reaction with an activation energy of 100−115 kJ mol^{-1}, which enables a fast exchange above the melting temperature of PP. In practice, the first reaction step is to functionalize PP with MA via a radical reaction in a melt compounder, as shown in Figure 16A. The cross-linking density is subsequently controlled by reacting pendant MA groups with a multifunctional thiol during the second step to produce exchangeable thioester bonds. The under- or above-stoichiometric ratio of the grafted MA and cross-linker enables the exchange reaction, as demonstrated in Figure 16B. The synthesis could not be performed in one step due to the strong reduction in the reactivity of MA if ring-opening with the cross-linker happened first. Varied amounts of the tetra-functional thiol cross-linker and the transesterification catalyst, TBD, were introduced into the compounder at 180 °C. The obtained vitrimers showed a

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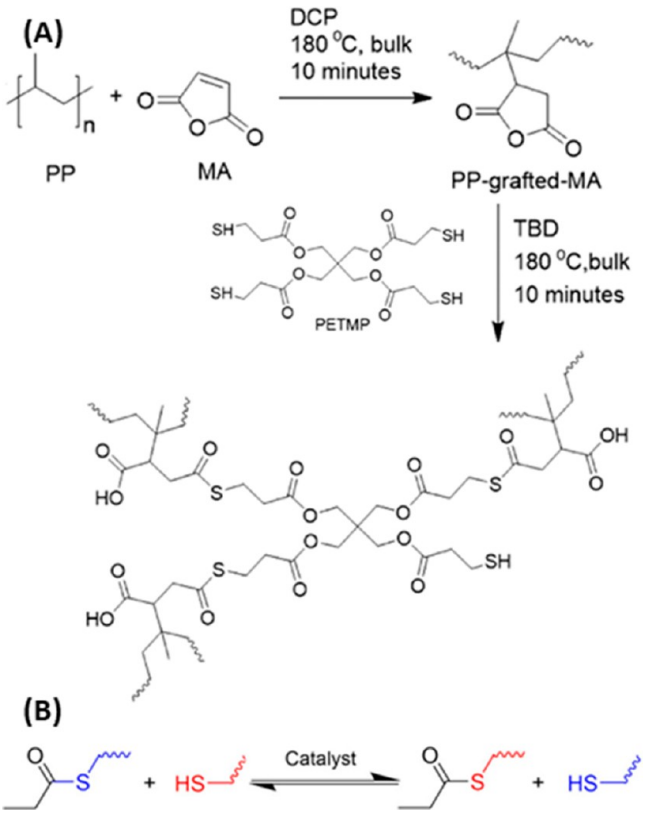

Figure 16. (A) Synthesis of PP vitrimers based on thiol−thioester exchange bonds: PP grafting with MA, followed by the introduction of tetra-thiol cross-linkers. (B) Thiol−thioester bond exchange. Reproduced with permission from ref 86. Copyright 2021 American Chemical Society.

monotonic decrease of crystallinity at larger cross-linking densities yet higher yield and breaking stress compared to those of pristine PP.

Diels−Alder is another reaction that is widely used for the construction of reversible networks. Picchioni and co-workers demonstrated the formation of a thermoreversible elastomer upon the integration of DA bonds in a commercial MA-functionalized EPR.[67] The pending anhydride groups were first modified with furfurylamine to graft furan groups onto the backbone, and furan groups were subsequently cross-linked with a bismaleimide as the DA cross-linker, as shown in Figure 17A. Accordingly, cross-links were dissociated at temperatures above 150 °C and could be rearranged upon annealing between 50 and 70 °C. Alternately, furan groups can be easily grafted to double bonds available in unsaturated rubbers such as PBd through a radical-induced thiol−ene reaction, as demonstrated by Shi and co-workers.[66] They functionalized PBd with furfuryl mercaptan in solution and subsequently formed DA bonds via the solution-mixing of the bismaleimide cross-linker, as shown in Figure 17B. Mechanical properties were easily tuned by adjusting the cross-linking degree accordingly.

5. PHASE SEPARATION

Generally, there is a strong difference in the polarity of the backbone and the reversible covalent cross-links in polyolefin vitrimers.[112] The phase separation term χN in the Flory−Huggins theory of polymer solution, where χ is the interaction parameter and N is the degree of polymerization, denotes that polar reversible cross-linkers have the affinity to segregate from the apolar polyolefins, which is amplified in longer chains. Additionally, when there is a wide distribution in the number of cross-links per chain, phase separation might be amplified. In contrast, the hindered polymeric dynamics of transiently cross-linked entangled polymer chains can compromise phase separation by limiting the accessibility of individual cross-links to each other even above the exchange temperature.[108,113] Nevertheless, the frozen network topology of polyolefin vitrimers is prone to contain phase-separated domains, the extent of which is determined by the compromise between thermodynamics and kinetics. Individual cross-links inside phase-separated domains have a higher chance to form misconnectivities such as loops and clusters compared to isolated cross-links in the bulk. Therefore, despite forming physical junctions with a high connectivity, phase-separated domains contribute less effectively to the network percolation and elasticity compared to the ones that are distributed in the bulk.[113,114] Therefore, any incentive that can discourage individual cross-links to phase separate or control the morphology to establish an ordered phase-separated structure[115] can promote not only the mechanical properties but also the recycling efficiency.

To account for that, Leibler and co-workers studied PE vitrimers with dioxaborolane maleimide reversible cross-links in both molten and semicrystalline states.[72] PE vitrimers demonstrated macroscopic phase separation into dioxaborolane maleimide-rich and maleimide-poor regions. Despite the crystallinity decreasing monotonically upon the grafting of dioxaborolane maleimide (PE-g) and the subsequent formation of reversible cross-links (PE-v), they formed a

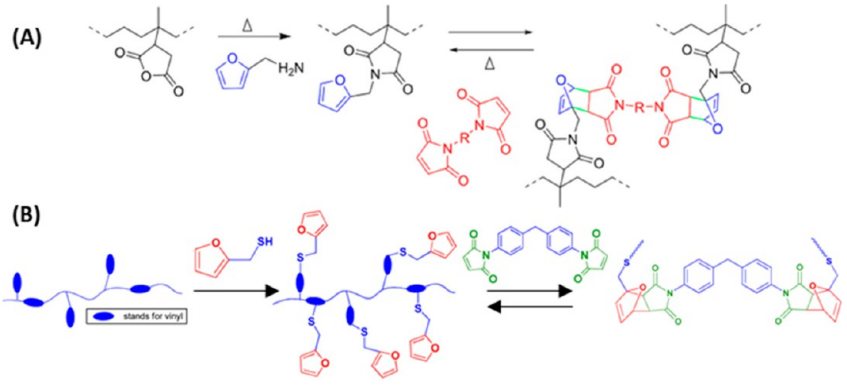

Figure 17. (A) Furan-group grafting and the formation of DA cross-links in a commercial EPR-g-MA elastomer. Reproduced with permission from ref 67. Copyright 2015 American Chemical Society. (B) Use of the thiol−ene reaction to graft furan and create reversible DA bonds in PBd. Reproduced with permission from ref 66. Copyright 2015 American Chemical Society.

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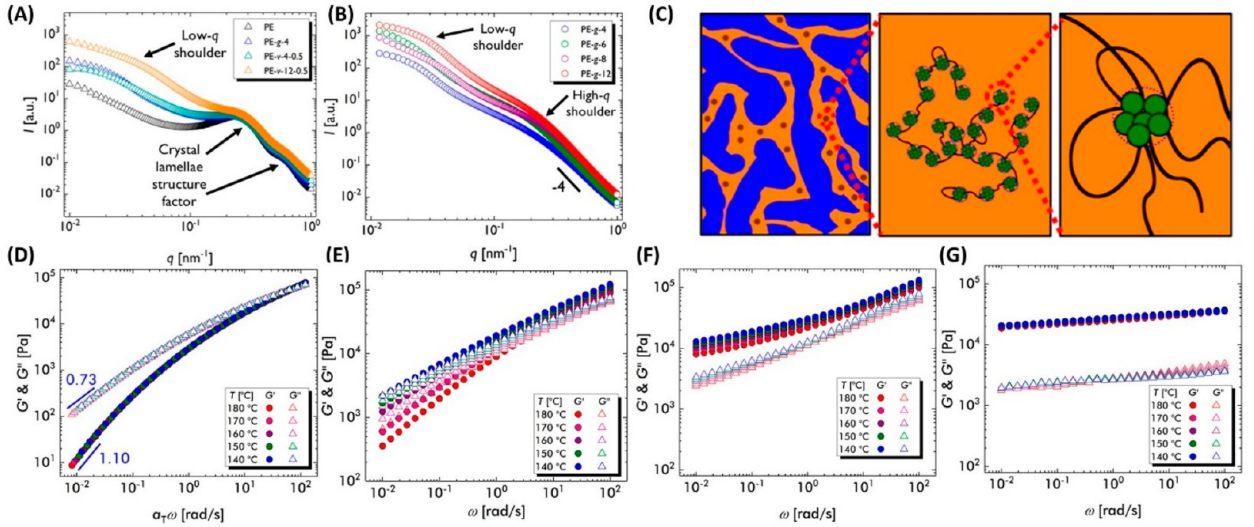

Figure 18. Comparison of the SAXS profiles of (A) neat PE, PE-g, and PE-v at 40 °C and (B) PE-g at 160 °C. (C) Schematic representation of the mesostructure, fractal structure, and aggregate structure in PE-g and PE-v samples. Reproduced with permission from ref 72. Copyright 2019 American Chemical Society. Dynamic moduli of (D) neat PE (master curve at 160 °C), (E) PE-g, (F) PE-v, and (G) the insoluble fraction of PE-v. Reproduced with permission from ref 71. Copyright 2020 American Chemical Society.

progressively opaquer film. The phase separation of the MA-grafted PE-g can also affect the homogeneous formation of dynamic cross-links during the reactive mixing. On the basis of SAXS studies, the insoluble phase contained aggregates of dioxaborolane grafts that were assembled into a fractal structure.[72] SAXS measurements confirmed that both PE-g and PE-v had semicrystalline and more complex structures compared to neat PE, as shown in Figure 18A and B, respectively. Moreover, wide-angle X-ray scattering (WAXS) analysis suggested that such long-range ordering does not alter the lamellar structure. Accordingly, they came up with a consistent image of the morphology of PE vitrimers, as shown in Figure 18C. Since all vitrimer samples investigated were turbid, macroscopic phase separation into rich and poor micrometer-length domains occurs in grafts or cross-linkers. At the nanoscale, the grafts or cross-links form small aggregates, as reflected by high-q shoulders in the SAXS patterns.

The macro- and microphase separation likely influences the dynamics of vitrimers over a wide range of time scales. Therefore, multiple rheological experiments must be employed to fully distinguish the influence of phase separation from that of individual cross-links. Stress-relaxation is the most commonly used measurement in vitrimer literature, but it is not suitable for systems whose stress decays by more than three decades. Time−temperature superposition (tTS) is also prone to fail with vitrimers, since generally the temperature dependence of polymeric dynamics and the exchange reactions vary significantly.[113] Therefore, the attainable time or frequency domain cannot be significantly broadened, specifically at longer times or shorter frequencies, respectively, by performing measurements at higher temperatures and applying the tTS law. As such, combining small-amplitude oscillatory shear with either stress-relaxation or creep measurement is widely used to better evaluate different aspects of chain relaxation.[116−118] In this regard, Leibler, and co-workers have shown that self-assembly and phase separation have significant impacts on the rheology and processability of vitrimers.[71] Rheological studies revealed that the soluble phase serves as a lubricant and binding agent, allowing the vitrimer to easily flow via a melt fracture−healing mechanism when subjected to a high stress.[71] To elucidate the role of self-assembly, they compared the rheological behavior of PE-g, PE-v, and the fraction of PE-v that was insoluble in the boiling xylene. While neat PE was thermorheologically simple and the corresponding master-curve of dynamic moduli demonstrated a terminal flow, as shown in Figure 18D, the PE-g sample showed a significant deviation from both thermorheological simplicity and terminal behavior, as shown in Figure 18E. In the absence of cross-links, this can only be attributed to the phase-separated morphology. Adding reversible cross-links further amplified these deviations toward the emergence of a low-frequency plateau modulus, as demonstrated in Figure 18F. Interestingly, the insoluble fraction of PE-v, despite having a plateau modulus lower than expected based on the entanglements, reflected characteristics of a chemical network with no sign of relaxation, as shown in Figure 18G. In contrast, the soluble portion, which was graft-poor, expressed flow behavior similar to that of neat PE. Therefore, rheological studies further support the microscopic image that was already developed based on SAXS results.[72]

6. APPLICATIONS OF POLYOLEFIN VITRIMERS

Vitrimers exhibit properties between thermosets and thermoplastics, as their cross-links can undergo percolation-conserving exchange reactions; therefore, they have found applications at the interface of these two classes of polymers. These properties range from recyclability, self-healing, adhesion, and an adjustable solid-to-liquid transition temperature, which are traditionally offered by thermoplastics, to resistance against environmental stress-cracking, creep resistance, and the shape-memory effect, which are better provided by thermosets.[5,9,90,119] Moreover, they have been considered as one of the main solutions to the current environmental issues with polymers by providing new resources for renewable thermosets on one hand and offering durable thermoplastics on the other hand. Additionally, introducing reversible bonds into polymer networks provides the potential for stimuli-responsiveness.[120] These features have provided a wide range of applications,

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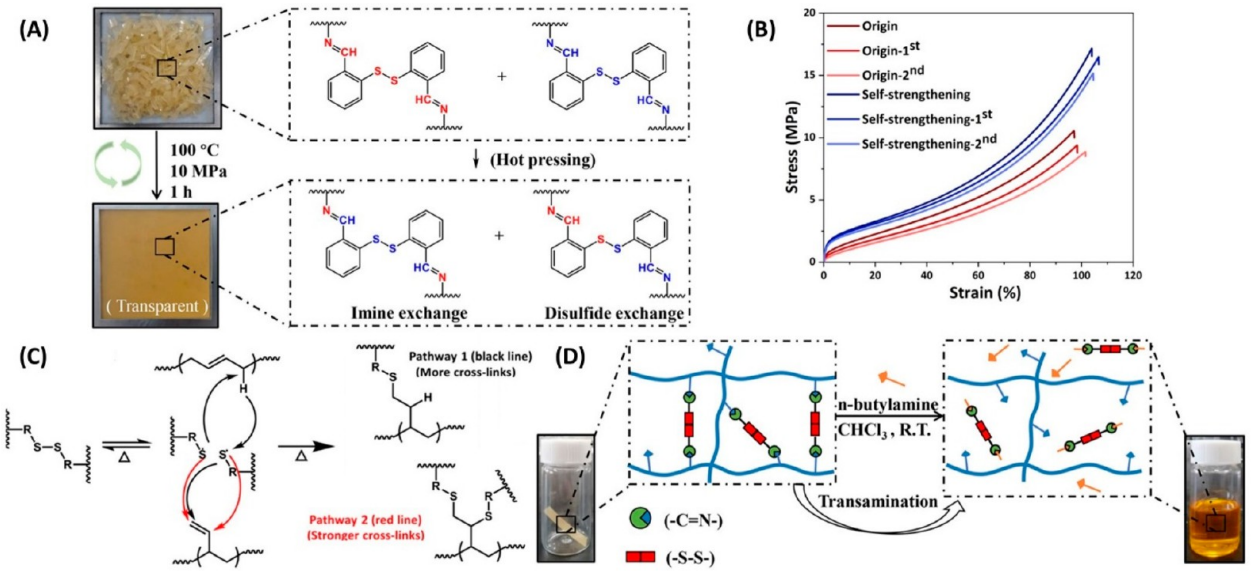

Figure 19. (A) Hot-press recycling of dual-dynamic PBd by the reformation of disulfide and imine bonds. (B) The corresponding tensile profiles demonstrate network strengthening. (C) Mechanism of self-strengthening by the formation of new permanent cross-links. (D) Chemical recycling by the dissolution of the network through exchange with monofunctional amine groups. Reproduced with permission from ref 76. Copyright 2022 American Chemical Society.

which are briefly reviewed in this section, with the focus on polyolefin-derivative vitrimers.

6.1. Recycling. Only 9% of plastic waste is recycled worldwide, of which polyolefins are some of the most frequently discarded.[121] Many different approaches have been proposed to increase the share of polyolefins in circular polymers, such as chemical recycling and the use of biorenewable resources; however, the apolar structure and the sensitivity of coordination polymerization methods have significantly limited the applicability of such approaches.[122−124] In contrast, some approaches for creating vitrimers are equally applicable to polyolefins compared to other polymers, as reviewed so far. The reformation of dynamic bonds after recycling results in the recovery of the original mechanical behavior, which can greatly compensate for the drop in mechanical properties of polyolefin thermoplastics during mechanical recycling, which frequently happens due to the inevitable thermo-oxidative chain scission reactions. Moreover, vitrimers can be reprocessed using conventional processing techniques. This advantage, which was solely afforded by thermoplastics up to now, allows traditional polyolefin elastomers to be recycled. Therefore, the application of the vitrimer concept to polyolefin thermoplastics and elastomers and any consequent success in their mechanical recycling, even a few percent, can significantly shift the statistics of polymer recycling toward a more sustainable future.

Evaluating mechanical properties of polyolefin vitrimers after multiple cycles of reprocessing is a common practice in almost every study on polyolefin vitrimers, as randomly mentioned throughout this Review. An important consideration is that the introduction of reversible bonds in the first place changes the mechanical properties of the pristine polymer, and what is expected to be recovered after multiple cycles of reprocessing are actually the modified properties, which may not meet the requirements of the intended application of the pristine polymer. For instance, the rubber-like behavior, as defined by a low modulus and high strain at break, normally shifts toward solid-like behavior, as characterized by high modulus and low strain at break, upon the increase of the cross-link density, as expected. Such a solid-like behavior and the recovery of that upon recycling may not fit the intended application of the pristine elastomer. Therefore, it is important to first clarify if the modification of such properties is in favor of the original application of the pristine polymer or, otherwise, if the modified properties are appealing for a new range of applications.

Polyolefin elastomers are composed of either unsaturated chains, such as diene-containing copolymers, or saturated ones, such as EPR and POE. This structural difference offers distinct routes for the grafting of functional groups, as reviewed so far. However, regardless of that, they all demonstrate a monotonic decrease of elongation at break and an enhanced modulus upon an increase in the fraction of reversible covalent cross-links. Nevertheless, in the presence of enough reversible bonds to restore a percolated network, mechanical properties can be retrieved.[48,49,66,76,84] For instance, Bai and co-workers have developed a self-straightening elastomer by integrating dual dynamic cross-links, composed of imine and disulfide units, into PBd chains.[76] Specifically, this material can be repeatedly cut and hot-pressed to form a transparent film due to the reformation of disulfide and imine bonds, as shown in Figure 19A. The corresponding tensile profile reflects even improved toughness due to the formation of new permanent cross-links, as demonstrated in Figure 19B. This is realized by the generation of phenysulfur radicals at high temperatures, which can further react with double bonds along chains and form extra cross-links, as outlined in Figure 19C. Moreover, this material can be recycled through liquid-phase recovery and ultimately dissolved in chloroform overnight, as shown in Figure 19D.

Similarly, Zhu and co-workers designed a simple and efficient scalable method for upcycling waste thermoplastic polyolefins into vitrimers based on internally catalyzed transesterification. As already mentioned in section 4.2, vitrimers were produced through a one-pot reaction that included grafting and cross-linking at the same time (see

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Figure 12). Specifically, they mixed postconsumer LDPE bags with MA, butanediol as the cross-linker, and DCP in a twin-screw extruder, as shown in Figures 20A and B. Although they

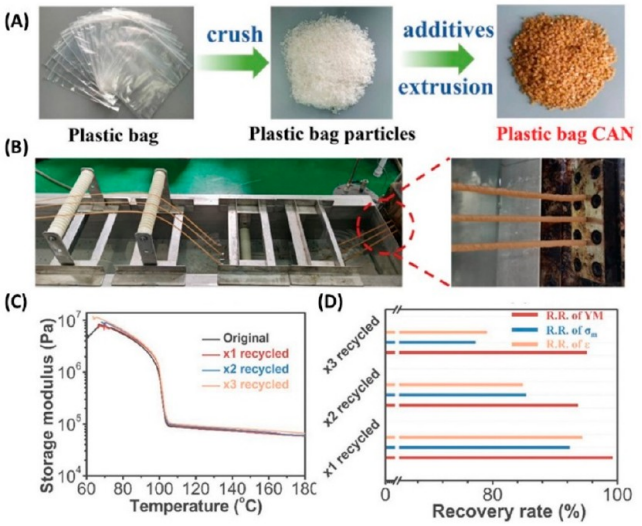

Figure 20. (A) Preparation of vitrimers from PE bags. (B) Vitrimer extrusion in an industrial-scale twin-screw extruder. (C) Storage modulus as a function of temperature for the original and recycled vitrimer. (D) Recovery rate (R.R.) of the Young modulus (YM) tensile strength (σm) and the elongation at break (ε) after three rounds of recycling. Reproduced with permission from ref 69. Copyright 2021 Royal Society of Chemistry.

were cross-linked, the vitrimers could be reprocessed multiple times at elevated temperatures through anhydride monoester transesterification. Even after three rounds of recycling, no significant drop in mechanical properties was observed as compared to the temperature dependence of the storage modulus and the recovery rate of the elastic modulus, elongation, and stress at break, as respectively shown in Figures 20C and D.

6.2. Self-Healing. Polymers, and specifically polyolefins, are vulnerable to the formation of craze and cracks that are normally caused by UV, heat, and stress during the end-use application. This is actually an important factor for the classification of HDPE pipe grades, e.g., a PE100 preserves a minimum required strength in a laboratory test that simulates 50 years of environmental stress cracking at 20 °C. Therefore, self-healing property can increase the service time of polyolefins and as such help save natural resources and raw materials. In the absence of external healing agents, self-healing is generally provided by the diffusion of chains through the crack and the reformation of transient bonds.[120,125] Therefore, there is a traditional trade-off between the healing capacity and mechanical properties, specifically in a semicrystalline polymer. To overcome this, some have suggested phase-separating the dynamic bonds, which are responsible for the fast healing, from the semicrystalline or hard segments, which provide the mechanical strength, so that the flexibility that is a prerequisite for healing efficiency does not undermine mechanical strength.[72,126] Similarly, multiple transient bonds with fast and slow dynamics can be applied in parallel, where the former helps self-healing and the latter improves the mechanical strength.[13,127−130] In this regard, Guan and co-workers have reported the self-healing properties of the semicrystalline 1,2-diol-containing polycyclooctene copolymers that were transiently cross-linked with two types of diphenylboronic ester cross-linkers with significantly different association kinetics.[54] They cut the solvent-cast films using a razor, kept the cut interfaces together for 1 min, allowed them to heal at 50 °C for 16 h. While the sample with stable cross-linkers showed minimal healing, the one with labile bonds almost quantitatively recovered the original mechanical properties, as shown in Figure 21A.[5]

Similarly, Guo and co-workers used a thermally initiated thiol−ene reaction to transiently cross-link SBR through mixing on an open two-roll mill and subsequent compression molding at 160 °C.[77] Samples were cut by a razor and put together to heal at different temperatures for various times.

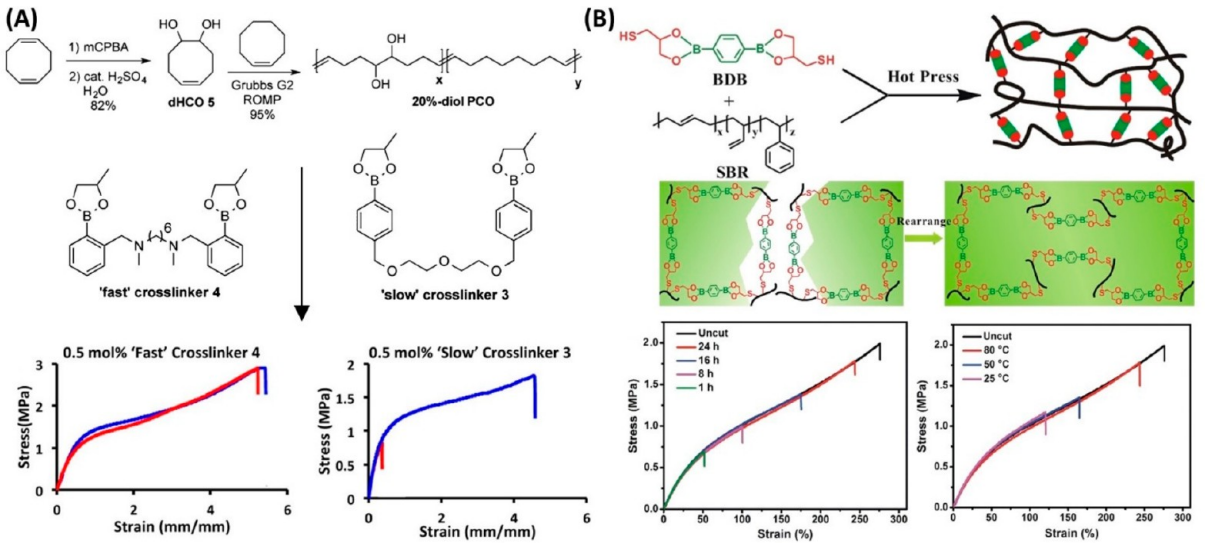

Figure 21. Self-healing properties upon transient cross-linking by boronic ester bonds. (A) The tensile strength of polycyclooctene vitrimers can be recovered upon healing for 16 h at 50 °C utilizing a fast-exchanging cross-link. Reproduced with permission from ref 54. Copyright 2015 American Chemical Society. (B) Progressively larger extents of healing can be obtained in SBR vitrimers at larger times and temperatures. Reproduced with permission from ref 77. Copyright 2018 American Chemical Society.

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Progressively larger extents of healing were obtained at longer times and higher temperatures, as shown in Figure 21B. This is realized by the transesterification reaction of boronic ester linkages, which results in the network rearrangement and bond shuffling at the interface of the cut surfaces, as schematically outlined in Figure 21B.

6.3. Adhesion. The nonpolar nature of polyolefins undermines their adhesion and printability, respectively, with polar surfaces and functional inks. However, different fields of application such as packaging and electronics require the welding of unlike polymers from various chemistries. The possibility to create a strong adhesion with permanently cross-linked polymers and composites is an important benefit of vitrimers.[5,9,131] Therefore, introducing dynamic covalent bonds into polyolefins is of prime interest for such applications. Accordingly, Leibler and co-workers reported that while a grafted copolymer is traditionally used to glue PMMA and PE, the dioxaborolane vitrimers of PMMA and PE can be easily and efficiently welded without the need for a tie layer.[5] In addition to the presence of pending polar dioxaborolanes, which brings some compatibility and adhesion between two polymers, the exchange reaction leads to the formation of covalent bridges across the interface and further enhances the adhesion, as illustrated in Figure 22A. For instance, after 10

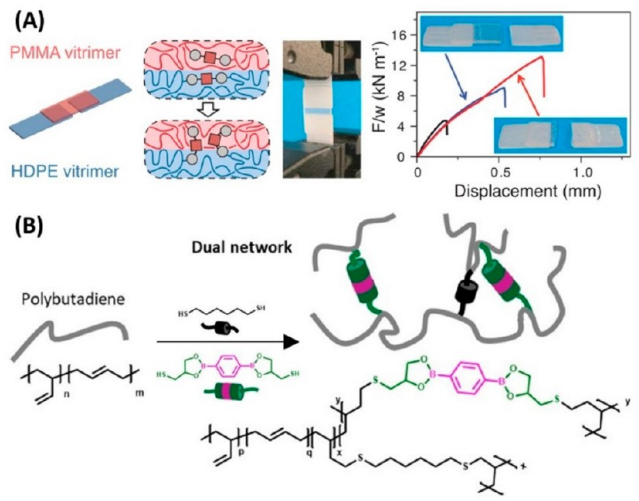

Figure 22. (A) Schematics of the lap-shear experiments of double-lap joints of PMMA/HDPE dioxaborolane thermoplastic precursors (10 min contact time, black) and PMMA/HDPE vitrimers (10 min contact (blue), interface failure; 20 min contact (red), bulk failure in PMMA). Reproduced with permission from ref 5. Copyright 2017 American Association for the Advancement of Science. (B) Dual-network PBd with permanent and transient dioxoborolane cross-links that demonstrate strong adhesion. Reproduced with permission from ref 55. Copyright 2019 American Chemical Society.

min of contact at 190 °C under 11 kPa pressure, the adhesion strength between PE and PMMA vitrimers in the lap-shear test was as high as 11.5 ± 4.5 kN m^{-1}, while after 20 min of welding the interfacial adhesion became so strong that fracture occurred in the bulk PMMA and not the interface.

Nicolay and co-workers have reported on the adhesion of PBd dual networks.[13,55] The material was prepared by the radical grafting of bisthiol dioxaborolane and 1,6-hexanedithiol with an unentangled PBd chain, which respectively formed dynamic and permanent cross-links, as shown in Figure 22B. Rectangular samples were overlaid and pressed for 2 min at 150 °C. The subsequent lap-shear experiments revealed that the interfacial adhesions were so strong that the failure occurred in the bulk. Even in the presence of the permanent cross-links that were required to form a percolated network, dual networks were fully recyclable and exhibited strong adhesion with short welding times.

6.4. Shape-Memory. The shape-memory property is the ability to recover the original shape from a programmed temporary shape upon the application of an external stimulus, such as heat, pH, light, etc.[132] Such stimuli-responsive materials have a great potential in applications such as sensors, actuators, and biomedical devices. The classical shape-memory effect is based on a molecularly locked structure as the reference, which is normally provided by permanent cross-links, and a temporary frozen structure, which can be provided by several stimuli-responsive transitions, such as the melting and glass transition temperatures in heat-responsive shape-memory materials or the dissociation of physical bonds in pH-responsive ones.[128] Multiple shape-memory behaviors can be also achieved in the presence of multiple switching segments, such as those with multiple distinct glass transitions or melting temperatures.[133,134] As such, thermoplastic polyolefins, which lack the reference cross-linked network, are incapable of restoring the original shape. The introduction of dynamic covalent bonds, however, offers the opportunity to introduce the shape-memory effect to polyolefins.[32,76,79,80] Although the dynamic topology switching of polyolefin vitrimers can result in plastic deformation and the alteration of the reference structure, if the deformation is applied fast enough and by a sufficiently low stress, no plastic creep will occur and good shape recovery can be expected. Moreover, due to the processability of vitrimers, the permanent reference structure can be reprogrammed at high temperatures.

On this account, many of the reports on the introduction of novel polyolefin vitrimers have also studied the shape-memory properties.[32,72,76,79,80] This is verified either qualitatively by observing the change in the shape upon careful thermal treatments or quantitatively under exact temperature and stress programs through dynamic mechanical analysis (DMA). For instance, HDPE vitrimers based on PTHF or PCL cross-links that could undergo exchange reaction upon transesterification, as shown in Figure 11C, have been reported to demonstrate multiple shape-memory effects stemming from their broad melting temperatures. Following DSC results, the first and the second programming temperatures were set at 130 and 110 °C, respectively under small loads of 0.03 and 0.1 MPa.[79] The temporary structure was fixed at 50 °C, as shown in Figure 23A. The first structure could be recovered at 120 °C, which is above the second programming temperature, and the permanent shape could be retrieved at 140 °C after all the crystals were melted. The entropic elasticity provided by the dynamic covalent bonds at temperatures that are yet below the onset of shuffling reactions promotes the recovery of the permanent shape. However, at temperatures beyond those, the permanent shape will be changed. A similar qualitative confirmation was obtained by extending a 3 cm vitrimer strip to 5 cm at 130 °C, followed by extending it to 10 cm at 110 °C and cooling it to 50 °C. The temporary 5 cm length could be recovered at 120 °C, and the permanent 3 cm length could be retrieved at 140 °C, as also shown in Figure 23A.

Similarly, the semicrystalline PEVA vitrimer based on exchangeable ester bonds, as shown in Figure 11E, also demonstrated visual memorable deformations.[80] A vitrimer

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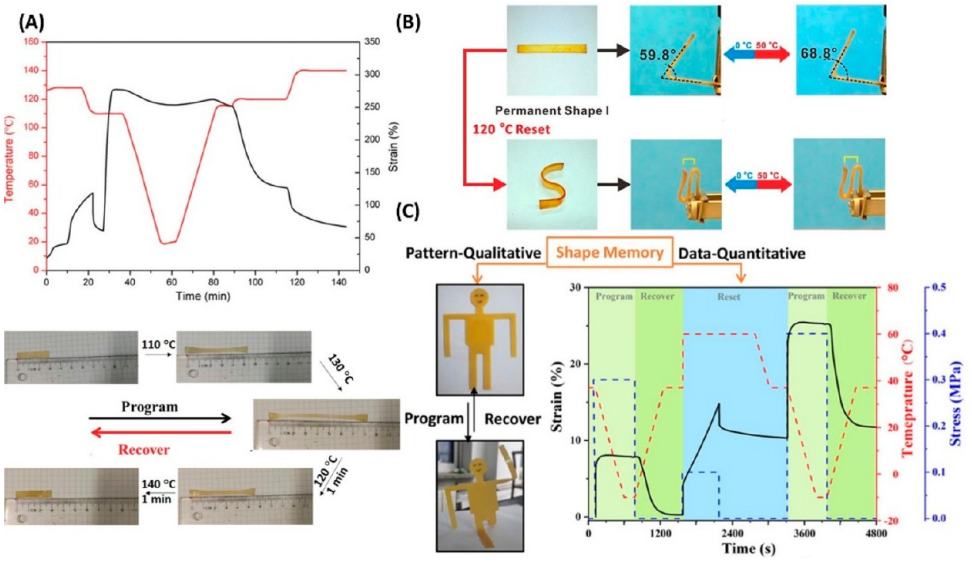

Figure 23. (A) Demonstration of the shape-memory effect in PE vitrimers via DMA and the qualitative observation of shape recovery. Reproduced with permission from ref 79. Copyright 2019 Wiley. (B) The reversible shape-memory effect in PEVA vitrimers, where the permanent V- or S-shape was set above the bond-exchange temperature and the angle or shape was changed by switching between 0 and 50 °C. Reproduced with permission from ref 80. Copyright 2018 American Chemical Society. (C) Qualitative observation and quantitative DMA data demonstrating the shape-memory behavior of PBd vitrimers. Reproduced with permission from ref 76. Copyright 2022 American Chemical Society.

strip was folded to a V-shape at 80 °C and held for 10 min, after which the sample was cooled to 0 °C and the external force was removed after 2 min. Subsequently, the sample angle could be autonomously changed from 59.8° to 68.8° upon heating to 50 °C and cooling to 0 °C, respectively, as shown in Figure 23B. Both angles showed minor increasing trends upon repeated the cycles, which can be attributed to the material relaxation that occurs after cyclic heating. The permanent shape could be changed into a S-shape upon heating at 120 °C for 30 min, and the new permanent shape could be transiently reprogrammed at 80 °C; the new shape demonstrated a similar reversible shape recovery via cyclic heating to 50 °C and cooling to 0 °C, as shown in Figure 23B. The reversible shape alteration was attributed to the melting of thin crystal lamellae, which could melt and reform between 50 and 0 °C. Similarly, Bai and co-workers have reported the shape-memory effect in PBd vitrimers with either imine-coordinated boroxine[83] or dual dynamic imine and disulfide cross-links,[76] as respectively shown in Figures 10B and 19A. The temporary shape was fixed above the T_g of the PBd vitrimers, which depends on the functionalization degree of the vitrimer, as shown in Figure 23C. In contrast, the permanent network could be reprogrammed at temperatures above the that for the onset of exchange reactions, which depends on the type of the exchange reaction but normally happens at temperatures much higher than T_g.

7. CONCLUSIONS AND PERSPECTIVE

While approaches to improving the mechanical recycling of polyolefins and replacing their fossil resources with renewable ones are advancing every day, vitrimers probably offer the most straightforward and versatile method for promoting the sustainability of polyolefins. They offer access to recyclable polyolefin elastomer by enabling cross-link exchange at high temperatures, which would be otherwise almost impossible to reprocess. Moreover, they can compensate for the loss of mechanical properties due to the thermo-oxidative degradation in thermoplastic polyolefins by reforming additional bonds at the service temperature. Nevertheless, due to the nonpolar nature of polyolefins, the feasible chemistries are limited and their application requires specific considerations. These chemistries, considerations, and their potential applications are reviewed in this Review. Despite the growing number of publications in this field, it is far from maturity, and many open questions have to be addressed before practical application in daily use. These questions span from (I) the underlying design and synthesis to (II) the reliable characterization and (III) the prospective application.

(I) While the necessity of using an associative-exchange mechanism to induce vitrimer-like behavior is questionable, revealing the true nature of many of the proposed reactions requires more in-depth investigations,[68] such as studies of the kinetics of the small-molecule equivalents or through theoretical simulations, rather than the simple evaluation of the Arrhenius dependence of viscosity on temperature.[11] The latter eventually provides a flow activation energy that significantly depends on the segmental motion of the polymer backbone[113] and therefore changes with the chain architecture and chemical composition. As such, the development of model polymeric systems based on telechelic and side-chain functionalized designs with the controlled placement of exchangeable bonds seems to become an emerging line of research in this field. Finally, the extent and effect of the synchronized radical-induced chain scission and chemical cross-linking during the postpolymerization formation of polyolefin vitrimers or their mechanical recycling or reprocessing, which affects various polyolefins differently, should be further elaborated.

(II) Many of the uncertainties with the characterization of transient polymer networks based on physical interactions are relevant in this context.[110] Specifically, the phase separation of polar cross-links from the apolar

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polyolefin backbone is a primary effect, the extent of which depends, on top of thermodynamics factors, on the method used to integrate the dynamic cross-links and the kinetics of phase separation, which is controlled by the lifetime of cross-links and precursor dynamics. The formation of the equilibrium phase-segregated structure before characterization or application is a necessity, which otherwise results in a severe time evolution of the structural properties. Moreover, the mutual effects of the crystallinity of thermoplastic polyolefins and the exchange reaction requires a more in-depth systematic study, as the countereffects of crystallinity suppression and the formation of exchangeable cross-links on the final properties are quite convoluted. Finally, vitrimers are expected to show glass-like creep over time, generating a long-term deviation of properties from true elastomers. Therefore, the inclusion of high-temperature, high-pressure tests that simulate the long-term properties of vitrimers seems to be a necessity from the industrial perspective.

(III) Following the last point, there is a traditional compromise between true recyclability and solid-like mechanical properties. Therefore, it is possible that not all polyolefin vitrimers can provide all the desired properties of polyolefin elastomers or thermoplastics. As such, it is necessary to either rethink the application range of the newly designed vitrimers or to fortify them for the desired application. Two promising approaches would be blending with other polymers and loading with (nano)fillers.[115,135] Many of the polyolefin products, even those with quite a similar chemical structures, such as high-density and low-density grades of polyethylene, are quite immiscible. That normally causes a serious issue for the sorting and individual recycling of each grade; therefore, polyolefin block copolymers have been recently developed and used as compatibilizers for the collective recycling of different polyolefin grades.[136−138] An alternative approach would be to mix them with vitrimers of various polyolefins to promote interfacial adhesion and improve the stability and mechanical properties of recycled blends.

Following these guidelines and considerations, and parallel to the introduction of more innovative polyolefin vitrimers, we are optimistic that further development in the industrialization of polyolefin vitrimers will significantly contribute to a more sustainable future.

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Notes

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REFERENCES

(1) Schneiderman, D. K.; Hillmyer, M. A. 50th anniversary perspective: There is a great future in sustainable polymers. *Macromolecules* **2017**, *50* (10), 3733−3749.

(2) Haque, F. M.; Ishibashi, J. S.; Lidston, C. A.; Shao, H.; Bates, F. S.; Chang, A. B.; Coates, G. W.; Cramer, C. J.; Dauenhauer, P. J.; Dichtel, W. R.; et al. Defining the Macromolecules of Tomorrow through Synergistic Sustainable Polymer Research. *Chem. Rev.* **2022**, *122* (6), 6322−6373.

(3) Fortman, D. J.; Brutman, J. P.; De Hoe, G. X.; Snyder, R. L.; Dichtel, W. R.; Hillmyer, M. A. Approaches to sustainable and continually recyclable cross-linked polymers. *ACS Sus. Chem. Eng.* **2018**, *6* (9), 11145−11159.

(4) Schyns, Z. O.; Shaver, M. P. Mechanical recycling of packaging plastics: A review. *Macromol. Rapid Commun.* **2021**, *42* (3), 2000415.

(5) Röttger, M.; Domenech, T.; van der Weegen, R.; Breuillac, A.; Nicolaÿ, R.; Leibler, L. High-performance vitrimers from commodity thermoplastics through dioxaborolane metathesis. *Science* **2017**, *356* (6333), 62−65.

(6) Kim, S.; Rahman, M. A.; Arifuzzaman, M.; Gilmer, D. B.; Li, B.; Wilt, J. K.; Lara-Curzio, E.; Saito, T. Closed-loop additive manufacturing of upcycled commodity plastic through dynamic cross-linking. *Sci. Adv.* **2022**, *8* (22), No. eabn6006.

(7) Kloxin, C. J.; Bowman, C. N. Covalent adaptable networks: smart, reconfigurable and responsive network systems. *Chem. Soc. Rev.* **2013**, *42* (17), 7161−7173.

(8) Luo, J.; Demchuk, Z.; Zhao, X.; Saito, T.; Tian, M.; Sokolov, A. P.; Cao, P.-F. Elastic vitrimers: Beyond thermoplastic and thermoset elastomers. *Matter* **2022**, *5* (5), 1391−1422.

(9) Capelot, M.; Montarnal, D.; Tournilhac, F.; Leibler, L. Metal-catalyzed transesterification for healing and assembling of thermosets. *J. Am. Chem. Soc.* **2012**, *134* (18), 7664−7667.

(10) Denissen, W.; Winne, J. M.; Du Prez, F. E. Vitrimers: permanent organic networks with glass-like fluidity. *Chem. Sci.* **2016**, *7* (1), 30−38.

(11) Scheutz, G. M.; Lessard, J. J.; Sims, M. B.; Sumerlin, B. S. Adaptable crosslinks in polymeric materials: resolving the intersection of thermoplastics and thermosets. *J. Am. Chem. Soc.* **2019**, *141* (41), 16181−16196.

(12) Van Zee, N. J.; Nicolaÿ, R. Vitrimers: Permanently crosslinked polymers with dynamic network topology. *Prog. Polym. Sci.* **2020**, *104*, 101233.

(13) Hammer, L.; Van Zee, N. J.; Nicolaÿ, R. Dually crosslinked polymer networks incorporating dynamic covalent bonds. *Polymers* **2021**, *13* (3), 396.

(14) Guerre, M.; Taplan, C.; Winne, J. M.; Du Prez, F. E. Vitrimers: directing chemical reactivity to control material properties. *Chem. Sci.* **2020**, *11* (19), 4855−4870.
(15) Winne, J. M.; Leibler, L.; Du Prez, F. E. Dynamic covalent chemistry in polymer networks: a mechanistic perspective. *Polym. Chem.* **2019**, *10* (45), 6091−6108.
(16) Elling, B. R.; Dichtel, W. R. Reprocessable cross-linked polymer networks: are associative exchange mechanisms desirable? *ACS Central Science* **2020**, *6* (9), 1488−1496.
(17) Odenwald, L.; Wimmer, F. P.; Mast, N. K.; Schußmann, M. G.; Wilhelm, M.; Mecking, S. Molecularly Defined Polyolefin Vitrimers from Catalytic Insertion Polymerization. *J. Am. Chem. Soc.* **2022**, *144* (29), 13226−13233.
(18) Jasinska-Walc, L.; Bouyahyi, M.; Duchateau, R. Potential of Functionalized Polyolefins in a Sustainable Polymer Economy: Synthetic Strategies and Applications. *Acc. Chem. Res.* **2022**, *55* (15), 1985−1996.
(19) Chen, M.; Chen, C. A Versatile Ligand Platform for Palladium- and Nickel-Catalyzed Ethylene Copolymerization with Polar Monomers. *Angew. Chem., Int. Ed.* **2018**, *57* (12), 3094−3098.
(20) Chen, M.; Chen, C. Direct and tandem routes for the copolymerization of ethylene with polar functionalized internal olefins. *Angew. Chem.* **2020**, *132* (3), 1222−1226.
(21) Tan, C.; Chen, C. Emerging palladium and nickel catalysts for copolymerization of olefins with polar monomers. *Angew. Chem.* **2019**, *131* (22), 7268−7276.
(22) Fortman, D. J.; Brutman, J. P.; Cramer, C. J.; Hillmyer, M. A.; Dichtel, W. R. Mechanically activated, catalyst-free polyhydroxyurethane vitrimers. *J. Am. Chem. Soc.* **2015**, *137* (44), 14019−14022.
(23) Dhers, S.; Vantomme, G.; Avérous, L. A fully bio-based polyimine vitrimer derived from fructose. *Green Chem.* **2019**, *21* (7), 1596−1601.
(24) Rekondo, A.; Martin, R.; de Luzuriaga, A. R.; Cabañero, G.; Grande, H. J.; Odriozola, I. Catalyst-free room-temperature self-healing elastomers based on aromatic disulfide metathesis. *Materials Horizons* **2014**, *1* (2), 237−240.
(25) Scott, T. F.; Schneider, A. D.; Cook, W. D.; Bowman, C. N. Photoinduced plasticity in cross-linked polymers. *Science* **2005**, *308* (5728), 1615−1617.
(26) Zhou, Y.; Goossens, J. G.; Sijbesma, R. P.; Heuts, J. P. Poly (butylene terephthalate)/glycerol-based vitrimers via solid-state polymerization. *Macromolecules* **2017**, *50* (17), 6742−6751.
(27) Demongeot, A.; Groote, R.; Goossens, H.; Hoeks, T.; Tournilhac, F.; Leibler, L. Cross-linking of poly (butylene terephthalate) by reactive extrusion using Zn (II) epoxy-vitrimer chemistry. *Macromolecules* **2017**, *50* (16), 6117−6127.
(28) Lu, Y.-X.; Tournilhac, F.; Leibler, L.; Guan, Z. Making insoluble polymer networks malleable via olefin metathesis. *J. Am. Chem. Soc.* **2012**, *134* (20), 8424−8427.
(29) Lessard, J. J.; Garcia, L. F.; Easterling, C. P.; Sims, M. B.; Bentz, K. C.; Arencibia, S.; Savin, D. A.; Sumerlin, B. S. Catalyst-free vitrimers from vinyl polymers. *Macromolecules* **2019**, *52* (5), 2105−2111.
(30) Ishibashi, J. S.; Kalow, J. A. Vitrimeric silicone elastomers enabled by dynamic meldrum's acid-derived cross-links. *ACS Macro Lett.* **2018**, *7* (4), 482−486.
(31) Caffy, F.; Nicolaÿ, R. Transformation of polyethylene into a vitrimer by nitroxide radical coupling of a bis-dioxaborolane. *Polym. Chem.* **2019**, *10* (23), 3107−3115.
(32) Kar, G. P.; Saed, M. O.; Terentjev, E. M. Scalable upcycling of thermoplastic polyolefins into vitrimers through transesterification. *J. Mater. Chem. A* **2020**, *8* (45), 24137−24147.
(33) Christensen, P. R.; Scheuermann, A. M.; Loeffler, K. E.; Helms, B. A. Closed-loop recycling of plastics enabled by dynamic covalent diketoenamine bonds. *Nat. Chem.* **2019**, *11* (5), 442−448.
(34) Denissen, W.; Droesbeke, M.; Nicolaÿ, R.; Leibler, L.; Winne, J. M.; Du Prez, F. E. Chemical control of the viscoelastic properties of vinylogous urethane vitrimers. *Nat. Commun.* **2017**, *8*, 14857.
(35) Liu, Y.; Tang, Z.; Chen, J.; Xiong, J.; Wang, D.; Wang, S.; Wu, S.; Guo, B. Tuning the mechanical and dynamic properties of imine bond crosslinked elastomeric vitrimers by manipulating the cross-linking degree. *Polym. Chem.* **2020**, *11* (7), 1348−1355.
(36) Menendez Rodriguez, G.; Díaz-Requejo, M. M.; Pérez, P. J. Metal-Catalyzed Postpolymerization Strategies for Polar Group Incorporation into Polyolefins Containing C−C, C= C, and Aromatic Rings. *Macromolecules* **2021**, *54* (11), 4971−4985.
(37) Ittel, S. D.; Johnson, L. K.; Brookhart, M. Late-metal catalysts for ethylene homo-and copolymerization. *Chem. Rev.* **2000**, *100* (4), 1169−1204.
(38) Guo, L.; Dai, S.; Sui, X.; Chen, C. Palladium and nickel catalyzed chain walking olefin polymerization and copolymerization. *ACS Catal.* **2016**, *6* (1), 428−441.
(39) Johnson, L. K.; Killian, C. M.; Brookhart, M. New Pd (II)-and Ni (II)-based catalysts for polymerization of ethylene and. alpha.-olefins. *J. Am. Chem. Soc.* **1995**, *117* (23), 6414−6415.
(40) Chen, Z.; Brookhart, M. Exploring ethylene/polar vinyl monomer copolymerizations using Ni and Pd α-diimine catalysts. *Acc. Chem. Res.* **2018**, *51* (8), 1831−1839.
(41) Maddah, Y.; Ahmadjo, S.; Mortazavi, S. M. M.; Sharif, F.; Hassanian-Moghaddam, D.; Ahmadi, M. Control over branching topology by introducing a dual catalytic system in coordinative chain transfer polymerization of olefins. *Macromolecules* **2020**, *53* (11), 4312−4322.
(42) Zhong, S.; Tan, Y.; Zhong, L.; Gao, J.; Liao, H.; Jiang, L.; Gao, H.; Wu, Q. Precision synthesis of ethylene and polar monomer copolymers by palladium-catalyzed living coordination copolymerization. *Macromolecules* **2017**, *50* (15), 5661−5669.
(43) Jandaghian, M. H.; Soleimannezhad, A.; Ahmadjo, S.; Mortazavi, S. M. M.; Ahmadi, M. Synthesis and characterization of isotactic poly (1-hexene)/branched polyethylene multiblock copolymer via chain shuttling polymerization technique. *Ind. Eng. Chem. Res.* **2018**, *57* (14), 4807−4814.
(44) de Espinosa, L. M.; Meier, M. A. Plant oils: The perfect renewable resource for polymer science?! *Eur. Polym. J.* **2011**, *47* (5), 837−852.
(45) He, Z.; Niu, H.; Zheng, N.; Liu, S.; Li, Y. Poly (ethylene-co-propylene)/poly (ethylene glycol) elastomeric hydrogels with thermoreversibly cross-linked networks. *Polym. Chem.* **2019**, *10* (35), 4789−4800.
(46) Wang, A.; Niu, H.; He, Z.; Li, Y. Thermoreversible cross-linking of ethylene/propylene copolymer rubbers. *Polym. Chem.* **2017**, *8* (31), 4494−4502.
(47) Liu, S.; Liu, X.; He, Z.; Liu, L.; Niu, H. Thermoreversible cross-linking of ethylene/propylene copolymers based on Diels−Alder chemistry: the cross-linking reaction kinetics. *Polym. Chem.* **2020**, *11* (36), 5851−5860.
(48) He, Z.; Niu, H.; Liu, L.; Xie, S.; Hua, Z.; Li, Y. Elastomeric polyolefin vitrimer: Dynamic imine bond cross-linked ethylene/propylene copolymer. *Polymer* **2021**, *229*, 124015.
(49) Yang, F.; Pan, L.; Ma, Z.; Lou, Y.; Li, Y.; Li, Y. Highly elastic, strong, and reprocessable cross-linked polyolefin elastomers enabled by boronic ester bonds. *Polym. Chem.* **2020**, *11* (19), 3285−3295.
(50) Wang, Z.; Gu, Y.; Ma, M.; Liu, Y.; Chen, M. Strengthening Polyethylene Thermoplastics through a Dynamic Covalent Networking Additive Based on Alkylboron Chemistry. *Macromolecules* **2021**, *54* (4), 1760−1766.
(51) Chung, T. Synthesis of functional polyolefin copolymers with graft and block structures. *Prog. Polym. Sci.* **2002**, *27* (1), 39−85.
(52) Chung, T. M. Functional polyolefins for energy applications. *Macromolecules* **2013**, *46* (17), 6671−6698.
(53) Jandaghian, M. H.; Ahmadjo, S.; Mortzavi, S. M. M.; Ahmadi, M. A mechanistic study on the synthesis of branched functional polyethylene through reactive co-polymer approach. *Appl. Organomet. Chem.* **2020**, *34* (4), No. e5496.
(54) Cromwell, O. R.; Chung, J.; Guan, Z. Malleable and self-healing covalent polymer networks through tunable dynamic boronic ester bonds. *J. Am. Chem. Soc.* **2015**, *137* (20), 6492−6495.

https://doi.org/10.1021/acs.chemmater.2c02853
Chem. Mater. XXXX, XXX, XXX−XXX

(55) Breuillac, A.; Kassalias, A.; Nicolaÿ, R. Polybutadiene vitrimers based on dioxaborolane chemistry and dual networks with static and dynamic cross-links. *Macromolecules* **2019**, *52* (18), 7102−7113.
(56) Ogden, W. A.; Guan, Z. Recyclable, strong, and highly malleable thermosets based on boroxine networks. *J. Am. Chem. Soc.* **2018**, *140* (20), 6217−6220.
(57) Lai, J. C.; Mei, J. F.; Jia, X. Y.; Li, C. H.; You, X. Z.; Bao, Z. A stiff and healable polymer based on dynamic-covalent boroxine bonds. *Adv. Mater.* **2016**, *28* (37), 8277−8282.
(58) Tanaka, R.; Tonoko, N.; Kihara, S.-i.; Nakayama, Y.; Shiono, T. Reversible star assembly of polyolefins using interconversion between boroxine and boronic acid. *Polym. Chem.* **2018**, *9* (27), 3774−3779.
(59) Noguchi, H.; Hojo, K.; Suginome, M. Boron-masking strategy for the selective synthesis of oligoarenes via iterative Suzuki− Miyaura coupling. *J. Am. Chem. Soc.* **2007**, *129* (4), 758−759.
(60) Tanaka, R.; Fujii, H.; Kida, T.; Nakayama, Y.; Shiono, T. Incorporation of Boronic Acid Functionality into Isotactic Polypropylene and Its Application as a Cross-Linking Point. *Macromolecules* **2021**, *54* (3), 1267−1272.
(61) Kondo, Y.; García-Cuadrado, D.; Hartwig, J. F.; Boaen, N. K.; Wagner, N. L.; Hillmyer, M. A. Rhodium-catalyzed, regiospecific functionalization of polyolefins in the melt. *J. Am. Chem. Soc.* **2002**, *124* (7), 1164−1165.
(62) Bae, C.; Hartwig, J. F.; Chung, H.; Harris, N. K.; Switek, K. A.; Hillmyer, M. A. Regiospecific side-chain functionalization of linear low-density polyethylene with polar groups. *Angew. Chem., Int. Ed.* **2005**, *44* (39), 6410−6413.
(63) Shin, J.; Chang, A. Y.; Brownell, L. V.; Racoma, I. O.; Ozawa, C. H.; Chung, H. Y.; Peng, S.; Bae, C. Hydrophilic graft modification of a commercial crystalline polyolefin. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46* (11), 3533−3545.
(64) Jo, T. S.; Yang, M.; Brownell, L. V.; Bae, C. Synthesis of quaternary ammonium ion-grafted polyolefins via activation of inert C−H bonds and nitroxide mediated radical polymerization. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47* (18), 4519−4531.
(65) Wagner, C. B.; Studer, A. Oxidation of alkylcatecholboranes with functionalized nitroxides for chemical modification of cyclohexene, perallylated polyglycerol and of poly (butadiene). *Eur. J. Org. Chem.* **2010**, *2010*, 5782−5786.
(66) Bai, J.; Li, H.; Shi, Z.; Yin, J. An eco-friendly scheme for the cross-linked polybutadiene elastomer via thiol−ene and Diels−Alder click chemistry. *Macromolecules* **2015**, *48* (11), 3539−3546.
(67) Polgar, L.; Van Duin, M.; Broekhuis, A.; Picchioni, F. Use of Diels−Alder chemistry for thermoreversible cross-linking of rubbers: the next step toward recycling of rubber products? *Macromolecules* **2015**, *48* (19), 7096−7105.
(68) Delahaye, M.; Winne, J. M.; Du Prez, F. E. Internal catalysis in covalent adaptable networks: phthalate monoester transesterification as a versatile dynamic cross-linking chemistry. *J. Am. Chem. Soc.* **2019**, *141* (38), 15277−15287.
(69) Wang, S.; Ma, S.; Qiu, J.; Tian, A.; Li, Q.; Xu, X.; Wang, B.; Lu, N.; Liu, Y.; Zhu, J. Upcycling of post-consumer polyolefin plastics to covalent adaptable networks via in situ continuous extrusion cross-linking. *Green Chem.* **2021**, *23* (8), 2931−2937.
(70) Peng, L.-M.; Xu, Z.; Wang, W.-Y.; Zhao, X.; Bao, R.-Y.; Bai, L.; Ke, K.; Liu, Z.-Y.; Yang, M.-B.; Yang, W. Leakage-Proof and Malleable Polyethylene Wax Vitrimer Phase Change Materials for Thermal Interface Management. *ACS Appl. Energy Mater.* **2021**, *4* (10), 11173−11182.
(71) Ricarte, R. G.; Tournilhac, F.; Cloître, M.; Leibler, L. Linear viscoelasticity and flow of self-assembled vitrimers: The case of a polyethylene/dioxaborolane system. *Macromolecules* **2020**, *53* (5), 1852−1866.
(72) Ricarte, R. G.; Tournilhac, F.; Leibler, L. Phase separation and self-assembly in vitrimers: Hierarchical morphology of molten and semicrystalline polyethylene/dioxaborolane maleimide systems. *Macromolecules* **2019**, *52* (2), 432−443.
(73) Maaz, M.; Riba-Bremerch, A.; Guibert, C.; Van Zee, N. J.; Nicolaÿ, R. Synthesis of Polyethylene Vitrimers in a Single Step: Consequences of Graft Structure, Reactive Extrusion Conditions, and Processing Aids. *Macromolecules* **2021**, *54* (5), 2213−2225.
(74) Xiao, Y.; Liu, P.; Wang, W.-J.; Li, B.-G. Dynamically Cross-Linked Polyolefin Elastomers with Highly Improved Mechanical and Thermal Performance. *Macromolecules* **2021**, *54* (22), 10381−10387.
(75) Wang, W.-Y.; Zha, X.-J.; Bao, R.-Y.; Ke, K.; Liu, Z.-Y.; Yang, M.-B.; Yang, W. Vitrimers of polyolefin elastomer with physically cross-linked network. *J. Polym. Res.* **2021**, *28*, 210.
(76) Yang, Y.; Huang, L.; Wu, R.; Niu, Z.; Fan, W.; Dai, Q.; Cui, L.; He, J.; Bai, C. Self-Strengthening, Self-Welding, Shape Memory, and Recyclable Polybutadiene-Based Material Driven by Dual-Dynamic Units. *ACS Appl. Mater. Interfaces* **2022**, *14* (2), 3344−3355.
(77) Chen, Y.; Tang, Z.; Zhang, X.; Liu, Y.; Wu, S.; Guo, B. Covalently cross-linked elastomers with self-healing and malleable abilities enabled by boronic ester bonds. *ACS Appl. Mater. Interfaces* **2018**, *10* (28), 24224−24231.
(78) Huang, Q.; Tang, Z.; Wang, D.; Wu, S.; Guo, B. Engineering segregated structures in a cross-linked elastomeric network enabled by dynamic cross-link reshuffling. *ACS Macro Lett.* **2021**, *10* (2), 231−236.
(79) Ji, F.; Liu, X.; Lin, C.; Zhou, Y.; Dong, L.; Xu, S.; Sheng, D.; Yang, Y. Reprocessable and recyclable crosslinked polyethylene with triple shape memory effect. *Macromol. Mater. Eng.* **2019**, *304* (3), 1800528.
(80) Gao, Y.; Liu, W.; Zhu, S. Reversible shape memory polymer from semicrystalline poly (ethylene-co-vinyl acetate) with dynamic covalent polymer networks. *Macromolecules* **2018**, *51* (21), 8956−8963.
(81) Zych, A.; Pinalli, R.; Soliman, M.; Vachon, J.; Dalcanale, E. Polyethylene vitrimers via silyl ether exchange reaction. *Polymer* **2020**, *199*, 122567.
(82) Tretbar, C. A.; Neal, J. A.; Guan, Z. Direct silyl ether metathesis for vitrimers with exceptional thermal stability. *J. Am. Chem. Soc.* **2019**, *141* (42), 16595−16599.
(83) Yang, Y.; Huang, L.; Wu, R.; Fan, W.; Dai, Q.; He, J.; Bai, C. Assembling of reprocessable polybutadiene-based vitrimers with high strength and shape memory via catalyst-free imine-coordinated boroxine. *ACS Appl. Mater. Interfaces* **2020**, *12* (29), 33305−33314.
(84) Zhang, H.; Wang, D.; Liu, W.; Li, P.; Liu, J.; Liu, C.; Zhang, J.; Zhao, N.; Xu, J. Recyclable polybutadiene elastomer based on dynamic imine bond. *J. Polym. Sci., Part A: Polym. Chem.* **2017**, *55* (12), 2011−2018.
(85) Tellers, J.; Pinalli, R.; Soliman, M.; Vachon, J.; Dalcanale, E. Reprocessable vinylogous urethane cross-linked polyethylene via reactive extrusion. *Polym. Chem.* **2019**, *10* (40), 5534−5542.
(86) Saed, M. O.; Lin, X.; Terentjev, E. M. Dynamic semicrystalline networks of polypropylene with thiol-anhydride exchangeable cross-links. *ACS Appl. Mater. Interfaces* **2021**, *13* (35), 42044−42051.
(87) Hall, D. G. *Boronic Acids: Preparation, Applications in Organic Synthesis and Medicine*; Wiley-VCH Verlab GmbH & Co.: Weinheim, Germany, 2005.
(88) Zheng, J.; Png, Z. M.; Ng, S. H.; Tham, G. X.; Ye, E.; Goh, S. S.; Loh, X. J.; Li, Z. Vitrimers: Current research trends and their emerging applications. *Mater. Today* **2021**, *51*, 586−625.
(89) Meng, F.; Saed, M. O.; Terentjev, E. M. Elasticity and relaxation in full and partial vitrimer networks. *Macromolecules* **2019**, *52* (19), 7423−7429.
(90) Montarnal, D.; Capelot, M.; Tournilhac, F.; Leibler, L. Silica-like malleable materials from permanent organic networks. *Science* **2011**, *334* (6058), 965−968.
(91) Stukenbroeker, T.; Wang, W.; Winne, J. M.; Du Prez, F. E.; Nicolaÿ, R.; Leibler, L. Polydimethylsiloxane quenchable vitrimers. *Polym. Chem.* **2017**, *8* (43), 6590−6593.
(92) Zhang, H.; Majumdar, S.; van Benthem, R. A.; Sijbesma, R. P.; Heuts, J. P. Intramolecularly catalyzed dynamic polyester networks using neighboring carboxylic and sulfonic acid groups. *ACS Macro Lett.* **2020**, *9* (2), 272−277.
(93) Liu, Y.; Ma, S.; Li, Q.; Wang, S.; Huang, K.; Xu, X.; Wang, B.; Zhu, J. Dynamic transfer auto-catalysis of epoxy vitrimers enabled by

https://doi.org/10.1021/acs.chemmater.2c02853
Chem. Mater. XXXX, XXX, XXX−XXX

the carboxylic acid/epoxy ratio based on facilely synthesized trifunctional monoesterified cyclic anhydrides. *Eur. Polym. J.* **2020**, *135*, 109881.
(94) Williamson, J. B.; Lewis, S. E.; Johnson, R. R., III; Manning, I. M.; Leibfarth, F. A. C− H functionalization of commodity polymers. *Angew. Chem., Int. Ed.* **2019**, *58* (26), 8654−8668.
(95) Nishimura, Y.; Chung, J.; Muradyan, H.; Guan, Z. Silyl ether as a robust and thermally stable dynamic covalent motif for malleable polymer design. *J. Am. Chem. Soc.* **2017**, *139* (42), 14881−14884.
(96) Mormann, W.; Wagner, T. Silylation of poly (vinyl alcohol) with hexamethyldisilazane in liquid ammonia. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33* (7), 1119−1124.
(97) Yang, J.; White, P. S.; Brookhart, M. Scope and mechanism of the iridium-catalyzed cleavage of alkyl ethers with triethylsilane. *J. Am. Chem. Soc.* **2008**, *130* (51), 17509−17518.
(98) Adachi, K.; Toyomura, S.; Miyakuni, Y.; Yamazaki, S.; Honda, K.; Hirano, T. Dioxomolybdenum (VI) and dioxotungsten (VI) complexes: efficient catalytic activity for crosslinking reaction in ethylene-vinyl acetate copolymer/alkoxysilane composites. *Polym. Adv. Technol.* **2015**, *26* (6), 597−605.
(99) Smith, M. B. *March'S Advanced Organic Chemistry: Reactions, Mechanisms, And Structure*, 8th ed.; Wiley, 2020.
(100) Belowich, M. E.; Stoddart, J. F. Dynamic imine chemistry. *Chem. Soc. Rev.* **2012**, *41* (6), 2003−2024.
(101) Whiteley, J. M.; Taynton, P.; Zhang, W.; Lee, S. H. Ultra-thin solid-state Li-ion electrolyte membrane facilitated by a self-healing polymer matrix. *Adv. Mater.* **2015**, *27* (43), 6922−6927.
(102) Taynton, P.; Ni, H.; Zhu, C.; Yu, K.; Loob, S.; Jin, Y.; Qi, H. J.; Zhang, W. Repairable woven carbon fiber composites with full recyclability enabled by malleable polyimine networks. *Adv. Mater.* **2016**, *28* (15), 2904−2909.
(103) Chao, A.; Negulescu, I.; Zhang, D. Dynamic covalent polymer networks based on degenerative imine bond exchange: tuning the malleability and self-healing properties by solvent. *Macromolecules* **2016**, *49* (17), 6277−6284.
(104) Taynton, P.; Yu, K.; Shoemaker, R. K.; Jin, Y.; Qi, H. J.; Zhang, W. Heat-or water-driven malleability in a highly recyclable covalent network polymer. *Adv. Mater.* **2014**, *26* (23), 3938−3942.
(105) Lei, Z. Q.; Xie, P.; Rong, M. Z.; Zhang, M. Q. Catalyst-free dynamic exchange of aromatic Schiff base bonds and its application to self-healing and remolding of crosslinked polymers. *J. Mater. Chem. A* **2015**, *3* (39), 19662−19668.
(106) Kuhl, N.; Bode, S.; Bose, R. K.; Vitz, J.; Seifert, A.; Hoeppener, S.; Garcia, S. J.; Spange, S.; Van Der Zwaag, S.; Hager, M. D.; et al. Acylhydrazones as reversible covalent crosslinkers for self-healing polymers. *Adv. Funct. Mater.* **2015**, *25* (22), 3295−3301.
(107) Wemyss, A. M.; Bowen, C.; Plesse, C.; Vancaeyzeele, C.; Nguyen, G. T.; Vidal, F.; Wan, C. Dynamic crosslinked rubbers for a green future: A material perspective. *Mater. Sci. Eng. R Rep.* **2020**, *141*, 100561.
(108) Ahmadi, M.; Jangizehi, A.; van Ruymbeke, E.; Seiffert, S. Deconvolution of the effects of binary associations and collective assemblies on the rheological properties of entangled side-chain supramolecular polymer networks. *Macromolecules* **2019**, *52* (14), 5255−5267.
(109) Jangizehi, A.; Ahmadi, M.; Seiffert, S. Dynamics of supramolecular associative polymer networks at the interplay of chain entanglement, transient chain association, and chain-sticker clustering. *J. Polym. Sci., Part B: Polym. Phys.* **2019**, *57* (18), 1209−1223.
(110) Jangizehi, A.; Ahmadi, M.; Seiffert, S. Emergence, evidence, and effect of junction clustering in supramolecular polymer materials. *Mater. Adv.* **2021**, *2* (5), 1425−1453.
(111) Denissen, W.; Rivero, G.; Nicolaÿ, R.; Leibler, L.; Winne, J. M.; Du Prez, F. E. Vinylogous urethane vitrimers. *Adv. Funct. Mater.* **2015**, *25* (16), 2451−2457.
(112) Chen, X.; Li, L.; Wei, T.; Torkelson, J. M. Reprocessable Polymer Networks Designed with Hydroxyurethane Dynamic Cross-links: Effect of Backbone Structure on Network Morphology, Phase Segregation, and Property Recovery. *Macromol. Chem. Phys.* **2019**, *220* (13), 1900083.
(113) Ahmadi, M.; Jangizehi, A.; Seiffert, S. Backbone polarity tunes sticker clustering in hydrogen-bonded supramolecular polymer networks. *Macromolecules* **2022**, *55* (13), 5514−5526.
(114) Rasid, I. M.; Do, C.; Holten-Andersen, N.; Olsen, B. D. Effect of sticker clustering on the dynamics of associative networks. *Soft Matter* **2021**, *17* (39), 8960−8972.
(115) Lessard, J. J.; Scheutz, G. M.; Sung, S. H.; Lantz, K. A.; Epps, T. H., III; Sumerlin, B. S. Block copolymer vitrimers. *J. Am. Chem. Soc.* **2020**, *142* (1), 283−289.
(116) Ahmadi, M.; Seiffert, S. Coordination geometry preference regulates the structure and dynamics of metallo-supramolecular polymer networks. *Macromolecules* **2021**, *54* (3), 1388−1400.
(117) Ahmadi, M.; Seiffert, S. Direct Evidence of Heteroleptic Complexation in the Macroscopic Dynamics of Metallo-supramolecular Polymer Networks. *Macromolecules* **2021**, *54* (15), 7113−7124.
(118) Entezam, M.; Abbasi, M.; Ahmadi, M. Theoretical correlation of linear and non-linear rheological symptoms of long-chain branching in polyethylenes irradiated by electron beam at relatively low doses. *Rheol. Acta* **2017**, *56* (9), 729−742.
(119) Nicolay, R.; Kamada, J.; Van Wassen, A.; Matyjaszewski, K. Responsive gels based on a dynamic covalent trithiocarbonate cross-linker. *Macromolecules* **2010**, *43* (9), 4355−4361.
(120) Zheng, N.; Xu, Y.; Zhao, Q.; Xie, T. Dynamic Covalent Polymer Networks: A Molecular Platform for Designing Functions beyond Chemical Recycling and Self-Healing. *Chem. Rev.* **2021**, *121* (3), 1716−1745.
(121) OECD. *Global Plastics Outlook: Economic Drivers, Environmental Impacts and Policy Options*. OECD Publishing: Paris, France, 2022.
(122) Coates, G. W.; Getzler, Y. D. Chemical recycling to monomer for an ideal, circular polymer economy. *Nat. Rev. Mater.* **2020**, *5* (7), 501−516.
(123) Zeng, M.; Lee, Y.-H.; Strong, G.; LaPointe, A. M.; Kocen, A. L.; Qu, Z.; Coates, G. W.; Scott, S. L.; Abu-Omar, M. M. Chemical Upcycling of Polyethylene to Value-Added α,ω-Divinyl-Functionalized Oligomers. *ACS Sustainable Chem. Eng.* **2021**, *9* (41), 13926−13936.
(124) Westlie, A. H.; Chen, E. Y. X.; Holland, C. M.; Stahl, S. S.; Doyle, M.; Trenor, S. R.; Knauer, K. M. Polyolefin Innovations toward Circularity and Sustainable Alternatives. *Macromol. Rapid Commun.* **2022**, 2200492.
(125) Ahmadi, M.; Ghanavati, M. Dynamics of self-healing supramolecular guanine-modified poly (n-butyl methacrylate-co-hydroxyethyl methacrylate) copolymers. *Polymer* **2020**, *211*, 123117.
(126) Chen, Y.; Kushner, A. M.; Williams, G. A.; Guan, Z. Multiphase design of autonomic self-healing thermoplastic elastomers. *Nat. Chem.* **2012**, *4* (6), 467−472.
(127) Li, C.-H.; Wang, C.; Keplinger, C.; Zuo, J.-L.; Jin, L.; Sun, Y.; Zheng, P.; Cao, Y.; Lissel, F.; Linder, C.; et al. A highly stretchable autonomous self-healing elastomer. *Nat. Chem.* **2016**, *8* (6), 618−624.
(128) Ahmadi, M.; Panahi, F.; Bahri-Laleh, N.; Sabzi, M.; Pareras, G.; Falcone, B.; Poater, A. pH-responsive gelation in metallo-supramolecular polymers based on the protic pyridinedicarboxamide ligand. *Chem. Mater.* **2022**, *34* (13), 6155−6169.
(129) Rodin, M.; Li, J.; Kuckling, D. Dually cross-linked single networks: Structures and applications. *Chem. Soc. Rev.* **2021**, *50* (14), 8147−8177.
(130) Zhang, B.; De Alwis Watuthanthrige, N.; Wanasinghe, S. V.; Averick, S.; Konkolewicz, D. Complementary dynamic chemistries for multifunctional polymeric materials. *Adv. Funct. Mater.* **2022**, *32* (8), 2108431.
(131) Chabert, E.; Vial, J.; Cauchois, J.-P.; Mihaluta, M.; Tournilhac, F. Multiple welding of long fiber epoxy vitrimer composites. *Soft Matter* **2016**, *12* (21), 4838−4845.
(132) Xie, T. Recent advances in polymer shape memory. *Polymer* **2011**, *52* (22), 4985−5000.

https://doi.org/10.1021/acs.chemmater.2c02853
Chem. Mater. XXXX, XXX, XXX−XXX

(133) Behl, M.; Razzaq, M. Y.; Lendlein, A. Multifunctional shape-memory polymers. *Adv. Mater.* **2010**, *22* (31), 3388−3410.
(134) Xie, T. Tunable polymer multi-shape memory effect. *Nature* **2010**, *464* (7286), 267−270.
(135) Schenk, V.; Labastie, K.; Destarac, M.; Olivier, P.; Guerre, M. Vitrimer composites: Current state and future challenges. *Mater. Adv.* **2022**, *3* (22), 8012−8029.
(136) Eagan, J. M.; Xu, J.; Di Girolamo, R.; Thurber, C. M.; Macosko, C. W.; LaPointe, A. M.; Bates, F. S.; Coates, G. W. Combining polyethylene and polypropylene: Enhanced performance with PE/i PP multiblock polymers. *Science* **2017**, *355* (6327), 814−816.
(137) Klimovica, K.; Pan, S.; Lin, T.-W.; Peng, X.; Ellison, C. J.; LaPointe, A. M.; Bates, F. S.; Coates, G. W. Compatibilization of i PP/HDPE Blends with PE-g-i PP Graft Copolymers. *ACS Macro Lett.* **2020**, *9* (8), 1161−1166.
(138) Xu, J.; Eagan, J. M.; Kim, S.-S.; Pan, S.; Lee, B.; Klimovica, K.; Jin, K.; Lin, T.-W.; Howard, M. J.; Ellison, C. J.; et al. Compatibilization of isotactic polypropylene (*i*PP) and high-density polyethylene (HDPE) with *i*PP−PE multiblock copolymers. *Macromolecules* **2018**, *51* (21), 8585−8596.

https://doi.org/10.1021/acs.chemmater.2c02853
Chem. Mater. XXXX, XXX, XXX−XXX