

Vitrimers: Using Dynamic Associative Bonds to Control Viscoelasticity, Assembly, and Functionality in Polymer Networks

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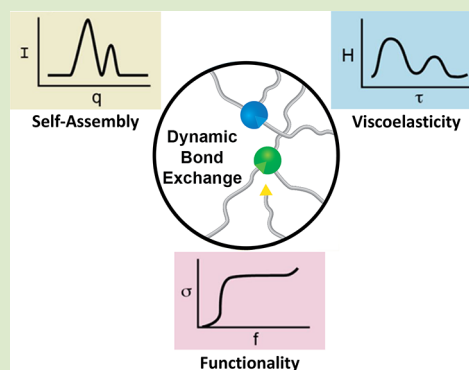
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ABSTRACT: Vitrimers have been investigated in the past decade for their promise as recyclable, reprocessable, and self-healing materials. In this Viewpoint, we focus on some of the key open questions that remain regarding how the molecular-scale chemistry impacts macroscopic physical chemistry. The ability to design temperature-dependent complex viscoelastic spectra with independent control of viscosity and modulus based on knowledge of the dynamic bond and polymer chemistry is first discussed. Next, the role of dynamic covalent chemistry on self-assembly is highlighted in the context of crystallization and nanophase separation. Finally, the ability of dynamic bond exchange to manipulate molecular transport and viscoelasticity is discussed in the context of various applications. Future directions leveraging dynamic covalent chemistry to provide insights regarding fundamental polymer physics as well as imparting functionality into polymers are discussed in all three of these highlighted areas.



Polymer networks containing dynamic covalent bonds are a promising platform for reconfigurable, recyclable, self-healing, and dissolvable polymers.^{1–6} Such systems are called covalent adaptable networks (CANs) regardless of the bond exchange mechanism, while the subclass of CANs containing associative dynamic covalent bonds are commonly called vitrimers. Vitrimers pose a plethora of fundamental questions about the role of molecular scale chemistry on the complex, temperature-dependent, viscoelastic response of dynamic polymer networks. The viscosity profile of vitrimers is distinct from both thermoplastics (sharp non-Arrhenius drop on heating above the glass temperature) and thermosets (no flow);⁷ however, their temperature-dependent moduli have been less investigated. Dynamic networks are a potentially transformative way to independently control the modulus (via cross-link density) and the viscosity (through bond exchange kinetics), as well as their temperature dependences, without changing polymer chemistry, using copolymerization strategies, or adding plasticizer/antiplasticizers or other fillers. Dynamic bonds also have the potential to impart functionality into polymers and can affect the ability of materials to self-assemble and crystallize. In this Viewpoint, we discuss how vitrimers can serve as a model platform to advance our understanding of three main areas: viscoelastic design, self-assembly, and functional polymers (Figure 1).

DYNAMIC BONDS DICTATE VISCOELASTIC RESPONSE OF VITRIMERS

Dynamic bonds can be either dissociative, where bonds break prior to exchange, or associative, where the dynamic bonds

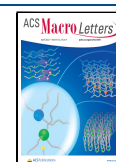
remain intact through the exchange event (Figure 2a).^{1,4–6,8} In Leibler and co-workers' pioneering work,⁹ a vitrimer has been defined as a polymer network with associative, dynamic covalent bonds that displayed an Arrhenius temperature dependence of viscosity approaching T_g . The past decade has seen a large variety of dynamic bonds incorporated into a range of polymer matrixes including commodity polymers like ethylene,¹⁰ and the Arrhenius behavior of stress relaxation times or viscosities has been observed with activation energies typically spanning ~30–160 kJ/mol,^{11–15} although values greater than 300 kJ/mol have been reported.¹⁶ Adding a catalyst decreases the relaxation time and can also change the activation energy (Figure 2b).^{11,14,17–27}

The Arrhenius dependence of viscosity or macroscopic stress relaxation time has also been observed in networks with dissociative bonds,^{11,28–34} raising the question of how the mechanism of bond exchange gives rise to the temperature-dependent viscosity. Du Prez and co-workers have found two distinct slopes in a vitrimer with temperature such that a lower activation energy was observed at lower temperature, corresponding to a breakdown of Arrhenius behavior.³⁵ A qualitatively similar phenomenon has also been observed in

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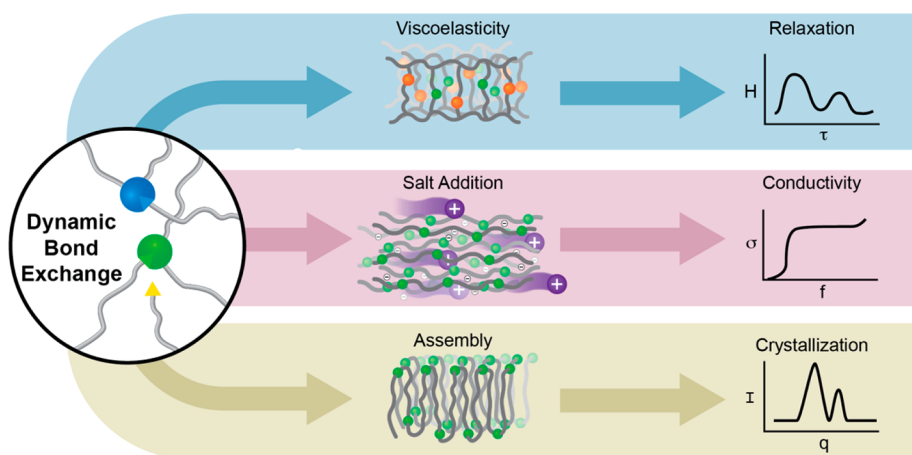


Figure 1. Dynamic bond exchange can impart functionality into polymer networks and control of both static and dynamic properties. Viscoelastic properties are tunable in vitrimers via control of the polymer backbone and cross-linker chemistry, density, and kinetically distinct cross-linkers (illustrated as orange and green spheres). Adding salt to vitrimers yields networks that are both conductive and self-healing (cations shown as purple spheres), which can improve battery electrolytes and actuators. In polymer networks that can self-assemble, the dynamic bond can facilitate assembly in otherwise trapped structures.

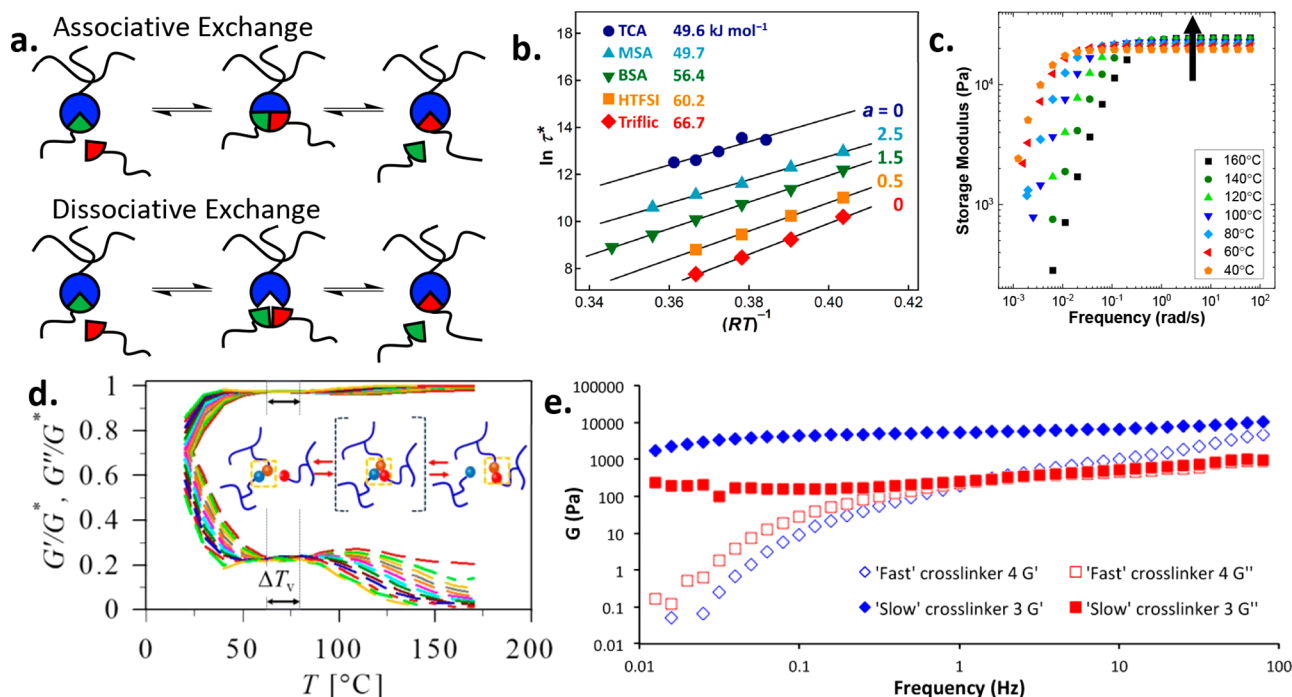


Figure 2. (a) Dynamic bonds can exchange in either an associative or dissociative manner, which may impact the resultant physics of the network. (b) Activation energies for vitrimers can vary with the type and loading of catalyst as seen in the case of Brønsted acids. Reprinted with permission from ref 26; copyright 2018 American Chemical Society. (c) The storage modulus of vitrimers is shown to increase with temperature as in permanently cross-linked networks due to entropic elasticity. Reprinted with permission from ref 36; copyright 2021 American Chemical Society. (d) T_v can be determined from a viscosity criterion or by a region of temperature-independent properties such as the storage and loss moduli. Reprinted with permission from ref 47; copyright 2020 American Chemical Society. (e) The selection of fast or slow bond exchange leads to differences in rheological properties, where the fast cross-linker shows a $G' = G''$ crossover and the slow network does not crossover on the experimental time scale. Such phenomena cannot yet be quantitatively predicted. Reprinted with permission from ref 24; copyright 2015 American Chemical Society.

PDMS vitrimers,³⁶ and recent work from Ricarte and co-workers has implicated the increasing role of polymer backbone dynamics as the cause for this change of slope.³⁷ Conversely, viscosity can show a stronger temperature dependence upon approaching T_g in some vitrimers, indicating that these effects are clearly nonuniversal and require further study.^{38,39} It has also been noted that many Arrhenius fits of vitrimers have been made over small temperature windows,

and these systems may show deviations if probed over a wider range.³⁶

Dynamic cross-links can also impact the modulus in two ways. The first is the well-known result that increasing the cross-link density increases the rubbery modulus. The second is through the temperature dependence of the modulus, because the network topology is conserved in vitrimers and, therefore, the modulus should increase upon heating as is

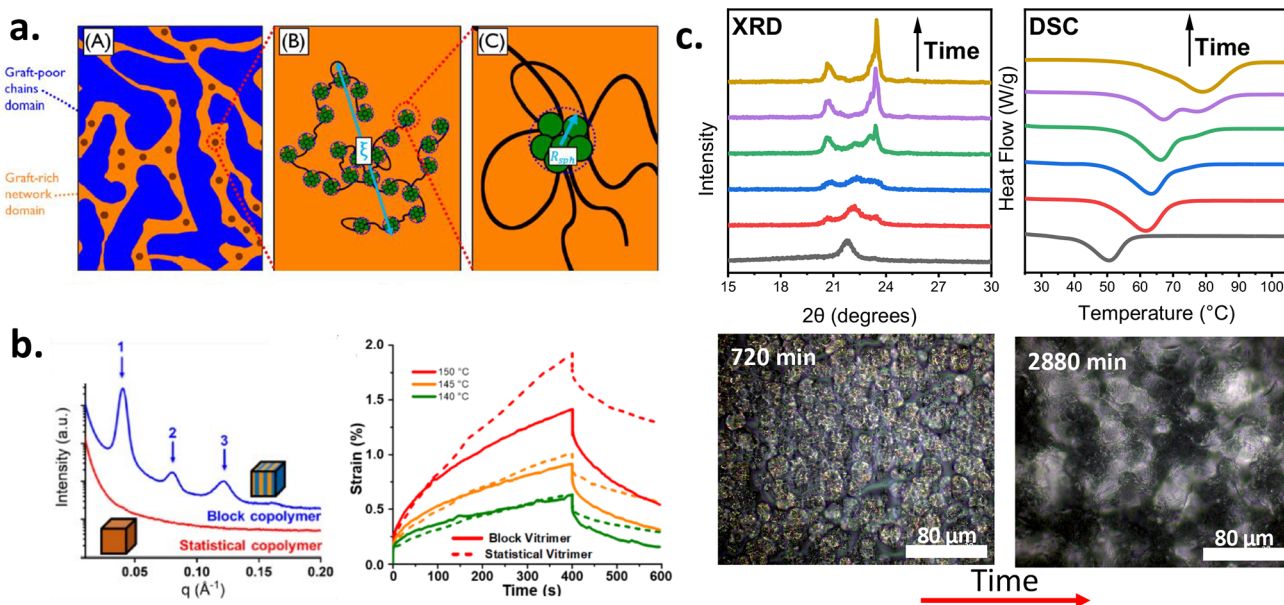


Figure 3. (a) Semicrystalline polyethylene vitrimers phase separate into hierarchical meso- and nanostructures due to the incompatibility of dynamic bond with the polymer. Reprinted with permission from ref 52; copyright 2019 American Chemical Society. (b) Dynamic bonds allow for linker rearrangements and crystallization, which is not observed in analogous permanent networks. Reprinted with permission from ref 59; copyright 2022 Royal Society of Chemistry. (c) Microphase-separated network structure contributes to the reduced macroscopic flow (creep) at longer time scales and larger deformations in a block vitrimer. Reprinted with permission from ref 72; copyright 2020 American Chemical Society.

observed in permanently cross-linked networks. Indeed, this entropic elasticity has been observed in vitrimers (Figure 2c) for a range of dynamic chemistries,^{34,36,39,40} while some dissociative CANs show softening.³⁰ It must be noted that there are exceptions where dissociative networks with large equilibrium binding constants can exhibit a small temperature window of rubbery stiffening⁴¹ because the number of dissociated bonds has only a negligible temperature dependence. From an applications standpoint, the decoupling of modulus and viscosity will be important for areas such as 3D printing,^{42,43} pressure sensitive adhesives,⁴⁴ and vibrational damping.⁴⁵

Another parameter frequently discussed in vitrimers is the topology freezing or vitrimer temperature, T_v , defined by Leibler as the value where the network is frozen due to the inability of dynamic bonds to exchange.⁹ An extrapolation of the viscosity to a value of 10^{12} Pa s is commonly used as the T_v criteria,²⁷ which is the same as that used for the glass transition in small molecules. If a vitrimer has a viscosity of 10^{12} Pa s, then the value of the storage or Young's modulus should distinguish whether the value is due to the glass transition (~ 1 GPa) or a frozen network (< 1 GPa). According to the Maxwell relation ($\eta = G\tau$, where η is viscosity, G is the storage modulus, and τ is the relaxation time), for a fixed viscosity, T_v can correspond to relaxation times, which vary by orders of magnitude depending on the modulus of the network, which can vary by orders of magnitude through the cross-link density. Thus, measurable relaxation times can be obtained even in frozen networks. As pointed out in a recent review article, T_v is also frequently determined from large extrapolations of viscosity (up to 100 K) where many factors may intervene (e.g., change of mechanism, glassy dynamics) to change the temperature dependence.⁴⁶ In recent work, Fang and Winter performed rheology measurements on an epoxy vitrimer that exhibited a 20 K region where material functions, such as the normalized storage modulus, had frequency-independent

behavior and a power law relaxation modulus (Figure 2d).⁴⁷ As an analogue to gelation rheology, this frequency independence has been assigned to a solid–solid transition that they have called T_v and which does not invoke a specific viscosity criterion. Recent simulation work has also defined T_v by finding the local minimum of the thermal expansion coefficient versus temperature.^{48,49} Further investigations into the significance of T_v , and how it is measured, are necessary for understanding how it may intervene in the temperature-dependent viscoelastic response of dynamic networks.

In addition to bulk relaxation, dynamic processes can impact polymer networks over a broad range of time and length scales. The quantitative relationship between the macroscopic time scale for self-healing or reprocessing of vitrimers and the time scale for bond exchange is not well understood. For example, Guan and co-workers have examined two cross-linkers for boronic ester networks that differed by the presence of a neighboring group that destabilizes the dynamic bond and leads to faster exchange reactions (Figure 2e).²⁴ Using small molecule model compounds and NMR, they have observed exchange rates that varied by 5 orders of magnitude. When the two cross-linkers are incorporated into a polymer network, the fast cross-linker shows a crossover of G' and G'' while the slow cross-linker does not crossover on the experimental time scale. In dissociative networks, the dynamic interactions are typically thought of as “sticky” groups that break and re-form on some time scale and lead to a delay in the onset of flow.⁵⁰ Recently, a variation of the sticky Rouse model has been applied to vitrimers to incorporate effects from bond exchange as well as the inherent dynamics of the polymer backbone.³⁷ A transition from a regime in which bond exchange and network strand relaxation control dynamics to one controlled purely by monomer friction is observed. The impact of dynamic bond sequence and placement along the backbone has also been described in this framework. The interplay of reaction kinetics, thermodynamics, and chain dynamics in vitrimers has also

been investigated recently by varying the degree of cross-linking and free small molecules to quantify deviations from Rouse-type behavior.⁵¹ While these works attempt to relate single bond exchange events to bulk responses, there is a lack of direct measurements of bond exchange kinetics in polymeric systems. Model small molecule experiments can be performed, but it is not clear if the kinetics or thermodynamics are preserved once the same bonds are incorporated into a network. In situ measurements of local dynamics using techniques such as dielectric spectroscopy, probe reorientation, or NMR will be needed to make the connection between these time and length scales.

An unresolved question for dynamic network classification is if they all sit on some spectrum ranging from linear stiffening with temperature ($G \sim \nu kT$, where G is the storage modulus (G), ν is the network strands per volume, k is the Boltzmann constant, and T is temperature) to decreasing modulus when network cross-links dissociate. More investigations into the rheological properties of associative and dissociative networks are needed, with an emphasis on temperature-dependent moduli and viscosity profiles. A systematic study between networks of identical polymer linkers cross-linked by using either dissociative or associative cross-linkers (with similar kinetics and activation energies) would provide much needed results on how their viscoelastic properties differ with temperature and time. Investigating the placement of dynamic bonds within the network, for example, in telechelic linkers or in strands with multiple cross-links per chain, will also be crucial to developing molecular-scale structure property relationships.

■ SELF-ASSEMBLY IN VITRIMERS

Much of the work to date on vitrimers has focused on their dynamic properties (such as stress relaxation times or viscosities) as well as the mechanical properties before and after recycling. Most vitrimers are studied in the amorphous state, but recent investigations have probed how dynamic bonds impact the nanostructure, including phase separation^{52–58} and crystallization.^{36,59–62} If vitrimers are slated to be replacements for commodity plastics, an improved understanding of assembly, crystallization, and phase separation is needed for the broad range of polymer applications. One of the earliest examples of this was in polyethylene vitrimers, which have been shown to form nanoscale clusters of the dioxaborolane cross-linking moieties within the incompatible matrix, which provides additional cross-linking and impacts the stress relaxation of the network (Figure 3a).^{52,58} Understanding when the dynamic bonds will phase separate from the matrix is critical for the interpretation of stress relaxation and self-healing investigations.

While the crystallization of polymers has been heavily investigated for decades, melting temperatures (T_m) have only been reported in a limited number of vitrimers based on PE,^{59,60} PDMS,³⁶ poly(butylene terephthalate),⁶¹ and poly(butylene succinate).⁶² It has recently been reported that the presence of dynamic bonds in vitrimers allows for crystallization, which is not possible in a permanent network with the same linker (Figure 3b).⁵⁹ The concomitant increases in percent crystallinity and enthalpy of fusion (relative to the permanent network) will lead to large effects on other properties such as thermal conductivity.⁶³ Quantitatively relating the bond exchange processes to the kinetics of crystallization and T_m evolution is an outstanding challenge.

The linking of two immiscible polymers to form a block copolymer (BCP) can lead to microphase separation in a wide array of nanostructures depending on the composition, architecture, and incompatibility of the blocks.^{64,65} This thermodynamically driven polymer self-assembly is a critical aspect of many current and emerging technologies including nanolithography,^{66,67} toughened rubbers and epoxies,⁶⁸ battery electrolytes,^{69,70} and photonic materials.⁷¹ Block copolymers containing one block that can participate in associative dynamic bonding have recently been investigated and can self-assemble at the nanoscale.⁷² The resulting self-assembled structures have been shown to reduce macroscopic flow (creep) in vitrimer block copolymer relative to a statistical copolymer with the same monomers and dynamic bond densities (Figure 3c). Such studies build upon the work of block polymers containing permanently cross-linked blocks that display rich physics distinct from linear AB type diblocks.^{73–75} It will be important to understand how bond exchange impacts the kinetics of assembly and alignment in these systems relative to permanently cross-linked diblocks, as well as linear block polymers, which can be investigated via shear alignment,⁷⁶ solvent annealing,⁷⁷ use of magnetic or electric fields,⁷⁸ and graphoepitaxy.^{79,80}

One of the open questions for vitrimers is how phase-separated domains and crystallites will impact dynamic bond exchange if they sit within or at the interface of the crystalline regions. The local environment of the bond may impact the stress relaxation and may lead to a reduction in creep of the network. An understanding of how the distribution of amorphous and crystalline regions impacts vitrimer static and dynamic properties is also currently lacking. Most vitrimers are composed of distributions in linker lengths, and the role of precise lengths may give rise to odd–even effects on T_m and crystallinity. Key scientific questions for dynamic diblocks center around the role of bond exchange on the assembly and alignment processes. In addition to the aforementioned cross-linked blocks, another iteration where a single dynamic bond is placed at the junction may lead to large effects on the kinetics of phase separation. Depending on the choice of dynamic bond, diblocks could be forced to only form AB linkages or to sample a combination of AA, AB, and BB in a binary system. Diblocks with a single dynamic junction may always favor macrophase separation, and a judicious combination of permanent and dynamic junctions may be required to stabilize the microphases. Understanding self-assembly in block copolymers with dynamic junctions could also inform the design of multistrand vitrimers leading to greater control and tunability of the static and dynamic properties. Knowledge of how to elicit or suppress macrophase separation in dynamic networks will be critical in these cases.

■ VITRIMERS FOR FUNCTIONAL MATERIALS

The tunability afforded in dynamic polymer networks makes them excellent candidates for a range of applications including electrolytes, damping materials, and stimuli-responsive polymers.^{81–84} In all cases, the control of viscosity, modulus, self-healing, and dissipation will be key to performance. In this section, a small subset of applications is discussed where vitrimers have begun to show promise in advancing the current state-of-the-art in materials design.

Solid electrolytes are often pursued as a safer alternative to liquids due to their reduced flammability. Ion-conducting permanent network electrolytes have shown impressive Li

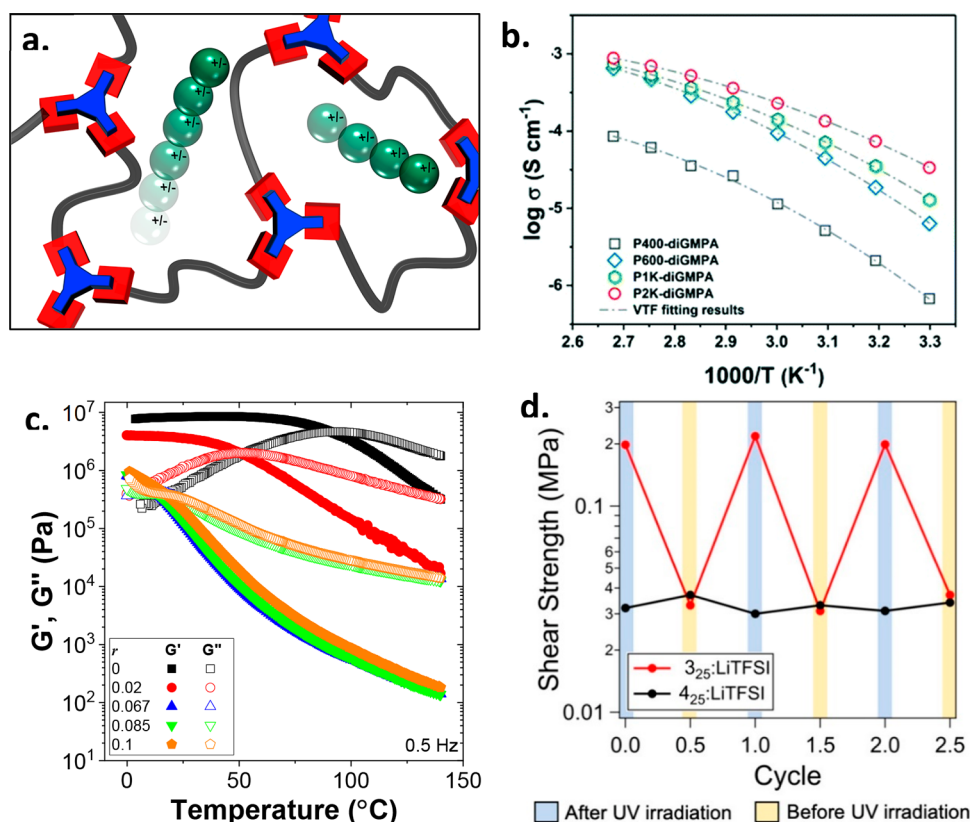


Figure 4. (a) Ions move through a dynamic polymer network where bond exchange or ion coordination can modify conductivity, viscosity, and modulus. (b) Dynamic PEO networks (red data) show increased conductivity when the mesh size is larger. Reprinted with permission from ref 89; copyright 2020 Royal Society of Chemistry. (c) PEO networks with boronic esters can coordinate with anions, leading to a drop in both viscosity and modulus with salt addition, in contrast to linear PEO electrolytes. Reprinted with permission from ref 40; copyright 2019 American Chemical Society. (d) Dynamic bond exchange in electrolytes can be triggered to generate reversible adhesion. Reprinted with permission from ref 88; copyright 2020 American Chemical Society.

dendrite suppression when cycled as Li-ion battery electrolytes even with a low shear modulus of $\sim 10^5$ Pa,⁸⁵ much softer than the glassy materials typically pursued.⁸⁶ It has been shown that vitrimers can have rubbery moduli $>10^5$ Pa and stiffen upon heating,^{20,36,39,40,87} reflecting a conserved network architecture that may mitigate dendrite propagation. Vitrimers can function as solid electrolytes due to the network structure, and dynamic bonds can facilitate ion transport compared to permanent networks of the same cross-link density as recently shown in poly(ethylene oxide) (PEO) networks.⁸⁸ Increasing the molecular weight of PEO between cross-links also leads to higher conductivity, even after accounting for changes in the network T_g (Figure 4b).^{88–90} For the dynamic networks that have been explored, a large variability in linker chemistry and cross-linking density exists, making it difficult to determine the direct impact of the exchange mechanism on ion mobility.

Salt addition can impact the rheological properties in addition to conductivity. Boronic esters have an empty p-orbital and are Lewis acids, which can coordinate with anions to form Lewis adducts.^{91–94} This leads to a significant change in the viscoelastic behavior with salt addition, as the bulk relaxation times decrease and bond exchange is accelerated as inferred from a drop in viscosity.^{40,90} Additionally, the modulus is substantially reduced as the linker strands compete with anions to interact with boronic esters (Figure 4c). The salt anion can undergo dissociative events with the boronic ester, and it is an open question if the linkers begin to mix associative and dissociative exchange. The drop in modulus is in contrast

to PEO networks with disulfide bonds, which stiffen upon salt addition.⁸⁸ The library of dynamic covalent chemistries is vast, and tuning ionic interactions with dynamic bonds can be used to control viscoelastic behavior and conductivity. Some dynamic bonds can coordinate with cations, such as vinyllogous urethanes,⁹⁵ and have recently been shown by Bao and co-workers to exhibit relaxations catalyzed by the cation of the salt.⁹⁶

A key open question for ionic vitrimers is how the time scales for molecular⁹⁷ or ionic^{98–100} hopping events compare to the bond exchange rates in vitrimers.^{11,46} Both time scales vary by many orders of magnitude with temperature, and systems can be designed where the time scales are comparable by selection of the dynamic chemistry and polymer T_g such that bond exchange may influence ionic transport. Another question is if the associative exchange mechanism of vitrimers can lead to a conserved topology such that dendrite suppression can be achieved akin to prior permanent network electrolyte studies.⁸⁵ In dense vitrimers, the mesh size can be made on the order of ~ 5 Å,⁹⁰ and in the case of salts like lithium bis(trifluoromethane sulfonamide) (LiTFSI), the anion (~ 8 Å) may be disproportionately hindered leading to improved transference numbers. Finally, the presence of anion coordinating dynamic bonds (boronic esters) may also lead to a greater fraction of current carried by the cation.

In the first section, we have discussed the design of vitrimer viscoelasticity through the choice of backbone, dynamic bond, sequence, and cross-link density. This knowledge is critical for

improving polymers for damping and dissipation applications. Historically, this has been pursued by tuning the segmental dynamics through T_g or copolymerization. When the peak frequency of a quantity such as $\tan \delta$ aligns with the frequency of a sound wave, damping occurs.⁴⁵ Control of the relaxation spectrum and $\tan \delta$ peaks has been demonstrated in soft hydrogels by using a combination of metal ions that lead to different exchange rates with organic ligands.¹⁰¹ Two $\tan \delta$ peaks have been observed in these metallogels (a dissociative dynamic network) when two different metal ions are used, but not in boronic ester hydrogels with two kinetically distinct dynamic bonds.¹⁰² Dry vitrimers have also used kinetically different bonds¹⁰³ and have shown either one or three modes depending on the difference between the bond relaxation time scales. Mixed networks with both associative and dissociative bonds have also been explored recently with mixed systems tending to have faster network relaxation times than the corresponding pure systems.^{104–107} Our understanding of how multiple dynamic bonds give rise to multiple peaks in a damping spectrum is still limited. Some work has implicated dynamic bonds as an efficient route to shockwave energy dissipation (~ 1 GPa peak pressure in ~ 10 ns),¹⁰⁸ where the dissipation increases as more dynamic bonds are incorporated into the network. More work is needed to make quantitative comparisons between bond exchange rates and the time scale of the input pressure wave. Precise selection of the dynamic bonds, polymer chemistry, and presence of multiple dynamic moieties could be utilized to design materials for a range of damping applications, in addition to the aforementioned T_g and copolymerization strategies, which will ultimately provide even greater tunability.

The dynamic nature of vitrimers also provides an ideal platform for designing responsive polymers. In one recent example, ionic vitrimers have been used as reversible adhesives (Figure 4d), where UV light reversibly triggers the bond exchange in dynamic networks leading to greater adhesion strength.⁸⁸ Vitrimers have also received recent attention as actuators,^{81,109–113} in many cases combining liquid crystalline elastomers with dynamic bonds. These systems can actuate either by heat or light stimuli and often operate as shape memory systems. Depending on the temperature, the dynamic bonds can be highly active or effectively static, leading to either plastic or elastic deformations, respectively. There exists a large design space for selecting the polymer backbone and dynamic chemistries to control the temperature of shape programming, or possibly the existence of multiple shape transitions. An ongoing push to incorporate multistimuli response¹¹³ will also allow for greater control of actuation.

CONCLUSION

This Viewpoint has explored three key areas of vitrimer design and functionality. Vitrimers open a vast rheological design space, with tunability not present in linear polymers, permanently cross-linked networks, or even dissociative dynamic networks that could be essential for unprecedented control of polymer modulus and viscosity. Key open questions remain, including the role of associative versus dissociative bonding on a broad range of macroscopic properties. The dynamic nature of vitrimers is also important for tuning and understanding self-assembly in crystallizable or multicomponent systems where heterogeneity may play a major role in structural and dynamic phenomena. For adoption into real-world applications, the interplay between polymer chemistry

and dynamic bonds should be leveraged to design next generation functional materials including electrolytes, damping materials, and stimuli-responsive systems.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Kloxin, C. J.; Bowman, C. N. Covalent adaptable networks: smart, reconfigurable and responsive network systems. *Chem. Soc. Rev.* **2013**, *42* (17), 7161–7173.
- (2) Denissen, W.; Winne, J. M.; Du Prez, F. E. Vitrimers: permanent organic networks with glass-like fluidity. *Chemical Science* **2016**, *7* (1), 30–38.
- (3) Yang, Y.; Xu, Y.; Ji, Y.; Wei, Y. Functional epoxy vitrimers and composites. *Prog. Mater. Sci.* **2021**, *120*, 100710.
- (4) 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.
- (5) Van Zee, N. J.; Nicolaÿ, R. Vitrimers: Permanently crosslinked polymers with dynamic network topology. *Prog. Polym. Sci.* **2020**, *104*, 101233–101233.
- (6) Guerre, M.; Taplan, C.; Winne, J. M.; Du Prez, F. E. Vitrimers: directing chemical reactivity to control material properties. *Chemical Science* **2020**, *11* (19), 4855–4870.
- (7) Ferry, J. D. *Viscoelastic properties of polymers*; John Wiley & Sons, 1980.

- (8) Krishnakumar, B.; Sanka, R. V. S. P.; Binder, W. H.; Parthasarathy, V.; Rana, S.; Karak, N. Vitrimers: Associative dynamic covalent adaptive networks in thermoset polymers. *Chemical Engineering Journal* **2020**, *385*, 123820.
- (9) Montarnal, D.; Capelot, M.; Tournilhac, F.; Leibler, L. Silica-Like Malleable Materials from Permanent Organic Networks. *Science* **2011**, *334* (6058), 965–968.
- (10) Röttger, M.; Domenech, T.; van der Weegen, R.; Breuillac, A.; Nicolay, R.; Leibler, L. High-performance vitrimers from commodity thermoplastics through dioxaborolane metathesis. *Science* **2017**, *356* (6333), 62–65.
- (11) Jourdain, A.; Asbai, R.; Anaya, O.; Chehimi, M. M.; Drockenmüller, E.; Montarnal, D. Rheological Properties of Covalent Adaptable Networks with 1,2,3-Triazolium Cross-Links: The Missing Link between Vitrimers and Dissociative Networks. *Macromolecules* **2020**, *53* (6), 1884–1900.
- (12) Han, J.; Liu, T.; Hao, C.; Zhang, S.; Guo, B.; Zhang, J. A Catalyst-Free Epoxy Vitrimer System Based on Multifunctional Hyperbranched Polymer. *Macromolecules* **2018**, *51* (17), 6789–6799.
- (13) Lessard, J. J.; Scheutz, G. M.; Hughes, R. W.; Sumerlin, B. S. Polystyrene-Based Vitrimers: Inexpensive and Recyclable Thermosets. *ACS Applied Polymer Materials* **2020**, *2* (8), 3044–3048.
- (14) Chen, X.; Li, L.; Wei, T.; Venerus, D. C.; Torkelson, J. M. Reprocessable Polyhydroxyurethane Network Composites: Effect of Filler Surface Functionality on Cross-link Density Recovery and Stress Relaxation. *ACS Appl. Mater. Interfaces* **2019**, *11* (2), 2398–2407.
- (15) Brutman, J. P.; Delgado, P. A.; Hillmyer, M. A. Polylactide Vitrimers. *ACS Macro Lett.* **2014**, *3* (7), 607–610.
- (16) Ruiz de Luzuriaga, A.; Solera, G.; Azcarate-Ascasua, I.; Boucher, V.; Grande, H.-J.; Rekondo, A. Chemical control of the aromatic disulfide exchange kinetics for tailor-made epoxy vitrimers. *Polymer* **2022**, *239*, 124457.
- (17) Zheng, N.; Fang, Z.; Zou, W.; Zhao, Q.; Xie, T. Thermoset Shape-Memory Polyurethane with Intrinsic Plasticity Enabled by Transcaramoylation. *Angew. Chem., Int. Ed.* **2016**, *55* (38), 11421–11425.
- (18) 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.
- (19) Zheng, H.; Liu, Q.; Lei, X.; Chen, Y.; Zhang, B.; Zhang, Q. A conjugation polyimide vitrimer: Fabrication and performance. *J. Polym. Sci., Part A: Polym. Chem.* **2018**, *56* (22), 2531–2538.
- (20) Denissen, W.; Rivero, G.; Nicolay, R.; Leibler, L.; Winne, J. M.; Du Prez, F. E. Vinylogous Urethane Vitrimers. *Adv. Funct. Mater.* **2015**, *25* (16), 2451–2457.
- (21) Ishibashi, J. S. A.; Kalow, J. A. Vitrimeric Silicone Elastomers Enabled by Dynamic Meldrum's Acid-Derived Cross-Links. *ACS Macro Lett.* **2018**, *7* (4), 482–486.
- (22) 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.
- (23) He, C.; Shi, S.; Wang, D.; Helms, B. A.; Russell, T. P. Poly(oxime-ester) Vitrimers with Catalyst-Free Bond Exchange. *J. Am. Chem. Soc.* **2019**, *141* (35), 13753–13757.
- (24) 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.
- (25) 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.
- (26) Self, J. L.; Dolinski, N. D.; Zayas, M. S.; Read de Alaniz, J.; Bates, C. M. Brønsted-Acid-Catalyzed Exchange in Polyester Dynamic Covalent Networks. *ACS Macro Lett.* **2018**, *7* (7), 817–821.
- (27) Capelot, M.; Unterlass, M. M.; Tournilhac, F.; Leibler, L. Catalytic Control of the Vitrimer Glass Transition. *ACS Macro Lett.* **2012**, *1* (7), 789–792.
- (28) Diaz, M. M.; Van Assche, G.; Maurer, F. H. J.; Van Mele, B. Thermophysical characterization of a reversible dynamic polymer network based on kinetics and equilibrium of an amorphous furan-maleimide Diels-Alder cycloaddition. *Polymer* **2017**, *120*, 176–188.
- (29) Polgar, L. M.; Kingma, A.; Roelfs, M.; van Essen, M.; van Duin, M.; Picchioni, F. Kinetics of cross-linking and de-cross-linking of EPM rubber with thermoreversible Diels-Alder chemistry. *Eur. Polym. J.* **2017**, *90*, 150–161.
- (30) Sheridan, R. J.; Bowman, C. N. A Simple Relationship Relating Linear Viscoelastic Properties and Chemical Structure in a Model Diels-Alder Polymer Network. *Macromolecules* **2012**, *45* (18), 7634–7641.
- (31) Kloxin, C. J.; Scott, T. F.; Bowman, C. N. Stress Relaxation via Addition-Fragmentation Chain Transfer in a Thiol-ene Photopolymerization. *Macromolecules* **2009**, *42* (7), 2551–2556.
- (32) Zhang, Y.; Broekhuis, A. A.; Picchioni, F. Thermally Self-Healing Polymeric Materials: The Next Step to Recycling Thermoset Polymers? *Macromolecules* **2009**, *42* (6), 1906–1912.
- (33) Adzima, B. J.; Aguirre, H. A.; Kloxin, C. J.; Scott, T. F.; Bowman, C. N. Rheological and Chemical Analysis of Reverse Gelation in a Covalently Cross-Linked Diels-Alder Polymer Network. *Macromolecules* **2008**, *41* (23), 9112–9117.
- (34) Elling, B. R.; Dichtel, W. R. Reprocessable Cross-Linked Polymer Networks: Are Associative Exchange Mechanisms Desirable? *ACS Central Science* **2020**, *6* (9), 1488–1496.
- (35) Guerre, M.; Taplan, C.; Nicolay, R.; Winne, J. M.; Du Prez, F. E. Fluorinated Vitrimer Elastomers with a Dual Temperature Response. *J. Am. Chem. Soc.* **2018**, *140* (41), 13272–13284.
- (36) Porath, L. E.; Evans, C. M. Importance of Broad Temperature Windows and Multiple Rheological Approaches for Probing Viscoelasticity and Entropic Elasticity in Vitrimers. *Macromolecules* **2021**, *54* (10), 4782–4791.
- (37) Ricarte, R. G.; Shanbhag, S. Unentangled Vitrimer Melts: Interplay between Chain Relaxation and Cross-link Exchange Controls Linear Rheology. *Macromolecules* **2021**, *54* (7), 3304–3320.
- (38) 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.
- (39) Soman, B.; Evans, C. M. Effect of precise linker length, bond density, and broad temperature window on the rheological properties of ethylene vitrimers. *Soft Matter* **2021**, *17* (13), 3569–3577.
- (40) Jing, B. B.; Evans, C. M. Catalyst-Free Dynamic Networks for Recyclable, Self-Healing Solid Polymer Electrolytes. *J. Am. Chem. Soc.* **2019**, *141* (48), 18932–18937.
- (41) Zhang, L.; Rowan, S. J. Effect of Sterics and Degree of Cross-Linking on the Mechanical Properties of Dynamic Poly(alkylurea-urethane) Networks. *Macromolecules* **2017**, *50* (13), 5051–5060.
- (42) Sydney Gladman, A.; Matsumoto, E. A.; Nuzzo, R. G.; Mahadevan, L.; Lewis, J. A. Biomimetic 4D printing. *Nat. Mater.* **2016**, *15* (4), 413–418.
- (43) Yuk, H.; Zhao, X. A New 3D Printing Strategy by Harnessing Deformation, Instability, and Fracture of Viscoelastic Inks. *Adv. Mater.* **2018**, *30* (6), 1704028.
- (44) Chang, E. P. Viscoelastic Windows of Pressure-Sensitive Adhesives. *J. Adhes.* **1991**, *34* (1–4), 189–200.
- (45) Sperling, L. H. Sound and Vibration Damping with Polymers. *Sound and Vibration Damping with Polymers*; American Chemical Society, 1990; Vol. 424, pp 5–22.
- (46) 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.
- (47) Fang, H.; Ye, W.; Ding, Y.; Winter, H. H. Rheology of the Critical Transition State of an Epoxy Vitrimer. *Macromolecules* **2020**, *53* (12), 4855–4862.
- (48) Perego, A.; Khabaz, F. Volumetric and Rheological Properties of Vitrimers: A Hybrid Molecular Dynamics and Monte Carlo Simulation Study. *Macromolecules* **2020**, *53* (19), 8406–8416.
- (49) Perego, A.; Khabaz, F. Effect of bond exchange rate on dynamics and mechanics of vitrimers. *J. Polym. Sci.* **2021**, *59* (21), 2590–2602.

- (50) Leibler, L.; Rubinstein, M.; Colby, R. H. Dynamics of reversible networks. *Macromolecules* **1991**, *24* (16), 4701–4707.
- (51) Wu, S.; Yang, H.; Xu, W.-S.; Chen, Q. Thermodynamics and Reaction Kinetics of Symmetric Vitrimers Based on Dioxaborolane Metathesis. *Macromolecules* **2021**, *54* (14), 6799–6809.
- (52) 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.
- (53) Breuillac, A.; Caffy, F.; Vialon, T.; Nicolaÿ, R. Functionalization of polyisoprene and polystyrene via reactive processing using azidoformate grafting agents, and its application to the synthesis of dioxaborolane-based polyisoprene vitrimers. *Polym. Chem.* **2020**, *11* (40), 6479–6491.
- (54) Ling, F.; Liu, Z.; Chen, M.; Wang, H.; Zhu, Y.; Ma, C.; Wu, J.; Huang, G. Compatibility driven self-strengthening during the radical-responsive remolding process of poly-isoprene vitrimers. *Journal of Materials Chemistry A* **2019**, *7* (44), 25324–25332.
- (55) 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.
- (56) Niu, W.; Zhang, Z.; Chen, Q.; Cao, P.-F.; Advincula, R. C. Highly Recyclable, Mechanically Isotropic and Healable 3D-Printed Elastomers via Polyurea Vitrimers. *ACS Materials Letters* **2021**, *3* (8), 1095–1103.
- (57) 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 Vitriimer Phase Change Materials for Thermal Interface Management. *ACS Applied Energy Materials* **2021**, *4* (10), 11173–11182.
- (58) 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.
- (59) Soman, B.; Go, Y. K.; Shen, C. T.; Leal, C.; Evans, C. M. Impact of dynamic covalent chemistry and precise linker length on crystallization kinetics and morphology in ethylene vitrimers. *Soft Matter* **2022**, *18*, 293.
- (60) Caffy, F.; Nicolay, R. Transformation of polyethylene into a vitriimer by nitroxide radical coupling of a bis-dioxaborolane. *Polym. Chem.* **2019**, *10* (23), 3107–3115.
- (61) 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-Vitriimer Chemistry. *Macromolecules* **2017**, *50* (16), 6117–6127.
- (62) Yin, Y.; Yang, J.; Meng, L. H. Preparation of poly(butylene succinate) vitriimer with thermal shape stability via transesterification reaction. *J. Appl. Polym. Sci.* **2021**, *138* (39), 51010.
- (63) Lv, G. X.; Soman, B.; Shan, N. S.; Evans, C. M.; Cahill, D. G. Effect of Linker Length and Temperature on the Thermal Conductivity of Ethylene Dynamic Networks. *ACS Macro Lett.* **2021**, *10* (9), 1088–1093.
- (64) Lodge, T. P. Block Copolymers: Long-Term Growth with Added Value. *Macromolecules* **2020**, *53* (1), 2–4.
- (65) Bates, F. S.; Hillmyer, M. A.; Lodge, T. P.; Bates, C. M.; Delaney, K. T.; Fredrickson, G. H. Multiblock Polymers: Panacea or Pandora's Box? *Science* **2012**, *336* (6080), 434–440.
- (66) Bates, C. M.; Seshimo, T.; Maher, M. J.; Durand, W. J.; Cushen, J. D.; Dean, L. M.; Blachut, G.; Ellison, C. J.; Willson, C. G. Polarity-Switching Top Coats Enable Orientation of Sub-10-nm Block Copolymer Domains. *Science* **2012**, *338* (6108), 775–779.
- (67) Bang, J.; Jeong, U.; Ryu, D. Y.; Russell, T. P.; Hawker, C. J. Block Copolymer Nanolithography: Translation of Molecular Level Control to Nanoscale Patterns. *Adv. Mater.* **2009**, *21* (47), 4769–4792.
- (68) Thompson, Z. J.; Hillmyer, M. A.; Liu, J.; Sue, H. J.; Dettloff, M.; Bates, F. S. Block Copolymer Toughened Epoxy: Role of Cross-Link Density. *Macromolecules* **2009**, *42* (7), 2333–2335.
- (69) Singh, M.; Odusanya, O.; Wilmes, G. M.; Eitouni, H. B.; Gomez, E. D.; Patel, A. J.; Chen, V. L.; Park, M. J.; Fragouli, P.; Iatrou, H.; Hadjichristidis, N.; Cookson, D.; Balsara, N. P. Effect of molecular weight on the mechanical and electrical properties of block copolymer electrolytes. *Macromolecules* **2007**, *40* (13), 4578–4585.
- (70) Bouchet, R.; Maria, S.; Meziane, R.; Aboulaich, A.; Lienafa, L.; Bonnet, J. P.; Phan, T. N. T.; Bertin, D.; Gigmès, D.; Devaux, D.; Denoyel, R.; Armand, M. Single-ion BAB triblock copolymers as highly efficient electrolytes for lithium-metal batteries. *Nat. Mater.* **2013**, *12* (5), 452–457.
- (71) Kang, Y.; Walish, J. J.; Gorishnyy, T.; Thomas, E. L. Broad-wavelength-range chemically tunable block-copolymer photonic gels. *Nat. Mater.* **2007**, *6* (12), 957–960.
- (72) 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.
- (73) Hahn, H.; Chakraborty, A. K.; Das, J.; Pople, J. A.; Balsara, N. P. Order-disorder transitions in cross-linked block copolymer solids. *Macromolecules* **2005**, *38* (4), 1277–1285.
- (74) Gomez, E. D.; Das, J.; Chakraborty, A. K.; Pople, J. A.; Balsara, N. P. Effect of cross-linking on the structure and thermodynamics of lamellar block copolymers. *Macromolecules* **2006**, *39* (14), 4848–4859.
- (75) Hahn, H.; Eitouni, H. B.; Balsara, N. P.; Pople, J. A. Responsive solids from cross-linked block copolymers. *Phys. Rev. Lett.* **2003**, *90* (15), 155505.
- (76) Newby, G. E.; Hamley, I. W.; King, S. M.; Martin, C. M.; Terrill, N. J. Structure, rheology and shear alignment of Pluronic block copolymer mixtures. *J. Colloid Interface Sci.* **2009**, *329* (1), 54–61.
- (77) Li, X.; Peng, J.; Wen, Y.; Kim, D. H.; Knoll, W. Morphology change of asymmetric diblock copolymer micellar films during solvent annealing. *Polymer* **2007**, *48* (8), 2434–2443.
- (78) Thurn-Albrecht, T.; DeRouchey, J.; Russell, T. P.; Kolb, R. Pathways toward electric field induced alignment of block copolymers. *Macromolecules* **2002**, *35* (21), 8106–8110.
- (79) Segalman, R. A.; Yokoyama, H.; Kramer, E. J. Graphoepitaxy of spherical domain block copolymer films. *Adv. Mater.* **2001**, *13* (15), 1152.
- (80) Bita, I.; Yang, J. K. W.; Jung, Y. S.; Ross, C. A.; Thomas, E. L.; Berggren, K. K. Graphoepitaxy of self-assembled block copolymers on two-dimensional periodic patterned templates. *Science* **2008**, *321* (5891), 939–943.
- (81) Yang, Y.; Wang, H.; Zhang, S.; Wei, Y.; He, X.; Wang, J.; Zhang, Y.; Ji, Y. Vitriimer-based soft actuators with multiple responsiveness and self-healing ability triggered by multiple stimuli. *Matter* **2021**, *4* (10), 3354–3365.
- (82) Wang, Y.; Zheng, R.; Luo, J.; Malik, H. A.; Wan, Z.; Jia, C.; Weng, X.; Xie, J.; Deng, L.; Yao, X. Self-healing dynamically cross linked versatile polymer electrolyte: A novel approach towards high performance, flexible electrochromic devices. *Electrochim. Acta* **2019**, *320*, 134489.
- (83) Jo, Y. H.; Li, S.; Zuo, C.; Zhang, Y.; Gan, H.; Li, S.; Yu, L.; He, D.; Xie, X.; Xue, Z. Self-Healing Solid Polymer Electrolyte Facilitated by a Dynamic Cross-Linked Polymer Matrix for Lithium-Ion Batteries. *Macromolecules* **2020**, *53* (3), 1024–1032.
- (84) 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.
- (85) Khurana, R.; Schaefer, J. L.; Archer, L. A.; Coates, G. W. Suppression of Lithium Dendrite Growth Using Cross-Linked Polyethylene/Poly(ethylene oxide) Electrolytes: A New Approach for Practical Lithium-Metal Polymer Batteries. *J. Am. Chem. Soc.* **2014**, *136* (20), 7395–7402.
- (86) Stone, G. M.; Mullin, S. A.; Teran, A. A.; Hallinan, D. T.; Minor, A. M.; Hexemer, A.; Balsara, N. P. Resolution of the Modulus versus Adhesion Dilemma in Solid Polymer Electrolytes for

Rechargeable Lithium Metal Batteries. *J. Electrochem. Soc.* **2012**, *159* (3), A222–A227.

(87) Snyder, R. L.; Fortman, D. J.; De Hoe, G. X.; Hillmyer, M. A.; Dichtel, W. R. Reprocessable Acid-Degradable Polycarbonate Vitrimers. *Macromolecules* **2018**, *51* (2), 389–397.

(88) Kato, R.; Mirmira, P.; Sookezian, A.; Grocke, G. L.; Patel, S. N.; Rowan, S. J. Ion-Conducting Dynamic Solid Polymer Electrolyte Adhesives. *ACS Macro Lett.* **2020**, *9* (4), 500–506.

(89) Li, S.; Zuo, C.; Zhang, Y.; Wang, J.; Gan, H.; Li, S.; Yu, L.; Zhou, B.; Xue, Z. Covalently cross-linked polymer stabilized electrolytes with self-healing performance via boronic ester bonds. *Polym. Chem.* **2020**, *11* (36), 5893–5902.

(90) Jing, B. B.; Mata, P.; Zhao, Q.; Evans, C. M. Effects of crosslinking density and Lewis acidic sites on conductivity and viscoelasticity of dynamic network electrolytes. *J. Polym. Sci.* **2021**, *59*, 2492.

(91) Zhu, Y.; Li, Y.; Bettge, M.; Abraham, D. P. Positive Electrode Passivation by LiDFOB Electrolyte Additive in High-Capacity Lithium-Ion Cells. *J. Electrochem. Soc.* **2012**, *159* (12), A2109–A2117.

(92) Galbraith, E.; James, T. D. Boron based anion receptors as sensors. *Chem. Soc. Rev.* **2010**, *39* (10), 3831–3842.

(93) Prakash Reddy, V.; Blanco, M.; Bugga, R. Boron-based anion receptors in lithium-ion and metal-air batteries. *J. Power Sources* **2014**, *247*, 813–820.

(94) Kato, Y.; Suwa, K.; Ikuta, H.; Uchimoto, Y.; Wakihara, M.; Yokoyama, S.; Yabe, T.; Yamamoto, M. Influence of Lewis acidic borate ester groups on lithium ionic conduction in polymer electrolytes. *J. Mater. Chem.* **2003**, *13* (2), 280–285.

(95) Schlessinger, R. H.; Li, Y. J.; VonLangen, D. J. Nonracemic syn-selective aldol reactions with a second-generation vinylogous urethane lithium enolate. *J. Org. Chem.* **1996**, *61* (10), 3226–3227.

(96) Lin, Y.; Chen, Y.; Yu, Z.; Huang, Z.; Lai, J.-C.; Tok, J. B. H.; Cui, Y.; Bao, Z. Reprocessable and Recyclable Polymer Network Electrolytes via Incorporation of Dynamic Covalent Bonds. *Chem. Mater.* **2022**, *34* (5), 2393–2399.

(97) Zhang, R.; Schweizer, K. S. Statistical Mechanical Theory of Penetrant Diffusion in Polymer Melts and Glasses. *Macromolecules* **2016**, *49* (15), 5727–5739.

(98) Mogurampelly, S.; Keith, J. R.; Ganesan, V. Mechanisms Underlying Ion Transport in Polymerized Ionic Liquids. *J. Am. Chem. Soc.* **2017**, *139* (28), 9511–9514.

(99) Diddens, D.; Heuer, A.; Borodin, O. Understanding the Lithium Transport within a Rouse-Based Model for a PEO/LiTFSI Polymer Electrolyte. *Macromolecules* **2010**, *43* (4), 2028–2036.

(100) Borodin, O.; Smith, G. D. Mechanism of Ion Transport in Amorphous Poly(ethylene oxide)/LiTFSI from Molecular Dynamics Simulations. *Macromolecules* **2006**, *39* (4), 1620–1629.

(101) Grindy, S. C.; Learsch, R.; Mozhdehi, D.; Cheng, J.; Barrett, D. G.; Guan, Z.; Messersmith, P. B.; Holten-Andersen, N. Control of hierarchical polymer mechanics with bioinspired metal-coordination dynamics. *Nat. Mater.* **2015**, *14* (12), 1210–1216.

(102) Yesilyurt, V.; Ayoob, A. M.; Appel, E. A.; Borenstein, J. T.; Langer, R.; Anderson, D. G. Mixed Reversible Covalent Crosslink Kinetics Enable Precise, Hierarchical Mechanical Tuning of Hydrogel Networks. *Adv. Mater.* **2017**, *29* (19), 1605947.

(103) El-Zaatari, B. M.; Ishibashi, J. S. A.; Kalow, J. A. Cross-linker control of vitrimer flow. *Polym. Chem.* **2020**, *11* (33), 5339–5345.

(104) Zhang, H.; Wang, D.; Wu, N. N.; Li, C. H.; Zhu, C. Z.; Zhao, N.; Xu, J. Recyclable, Self-Healing, Thermadaptable Triple-Shape Memory Polymers Based on Dual Dynamic Bonds. *ACS Appl. Mater. Interfaces* **2020**, *12* (8), 9833–9841.

(105) Chen, Y.; Tang, Z. H.; Liu, Y. J.; Wu, S. W.; Guo, B. C. Mechanically Robust, Self-Healable, and Reprocessable Elastomers Enabled by Dynamic Dual Cross-Links. *Macromolecules* **2019**, *52* (10), 3805–3812.

(106) Chen, M.; Zhou, L.; Wu, Y. P.; Zhao, X. L.; Zhang, Y. J. Rapid Stress Relaxation and Moderate Temperature of Malleability Enabled by the Synergy of Disulfide Metathesis and Carboxylate Trans-

esterification in Epoxy Vitrimers. *ACS Macro Lett.* **2019**, *8* (3), 255–260.

(107) Fortman, D. J.; Snyder, R. L.; Sheppard, D. T.; Dichtel, W. R. Rapidly Reprocessable Cross-Linked Polyhydroxyurethanes Based on Disulfide Exchange. *ACS Macro Lett.* **2018**, *7* (10), 1226.

(108) Lee, J.; Jing, B. B.; Porath, L. E.; Sottos, N. R.; Evans, C. M. Shock Wave Energy Dissipation in Catalyst-Free Poly-(dimethylsiloxane) Vitrimers. *Macromolecules* **2020**, *53* (12), 4741–4747.

(109) Chen, Q.; Li, Y.; Yang, Y.; Xu, Y.; Qian, X.; Wei, Y.; Ji, Y. Durable liquid-crystalline vitrimer actuators. *Chemical Science* **2019**, *10* (10), 3025–3030.

(110) Tang, D.; Zhang, L.; Zhang, X.; Xu, L.; Li, K.; Zhang, A. Bio-Mimetic Actuators of a Photothermal-Responsive Vitrimer Liquid Crystal Elastomer with Robust, Self-Healing, Shape Memory, and Reconfigurable Properties. *ACS Appl. Mater. Interfaces* **2022**, *14* (1), 1929–1939.

(111) Chen, Z.; Wang, J.; Qi, H. J.; Wang, T.; Naguib, H. E. Green and Sustainable Layered Chitin–Vitrimer Composite with Enhanced Modulus, Reprocessability, and Smart Actuator Function. *ACS Sustainable Chem. Eng.* **2020**, *8* (40), 15168–15178.

(112) Chen, Q.; Qian, X.; Xu, Y.; Yang, Y.; Wei, Y.; Ji, Y. Harnessing the Day–Night Rhythm of Humidity and Sunlight into Mechanical Work Using Recyclable and Reprogrammable Soft Actuators. *ACS Appl. Mater. Interfaces* **2019**, *11* (32), 29290–29297.

(113) Chen, Q.; Yu, X.; Pei, Z.; Yang, Y.; Wei, Y.; Ji, Y. Multi-stimuli responsive and multi-functional oligoaniline-modified vitrimers. *Chemical Science* **2017**, *8* (1), 724–733.