

Reprocessable Cross-Linked Polymer Networks: Are Associative Exchange Mechanisms Desirable?

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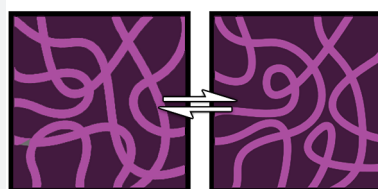
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ABSTRACT: Covalent adaptable networks (CANs) are covalently cross-linked polymers that may be reshaped via cross-linking and/or strand exchange at elevated temperatures. They represent an exciting and rapidly developing frontier in polymer science for their potential as stimuli-responsive materials and to make traditionally nonrecyclable thermosets more sustainable. CANs whose cross-links undergo exchange via associative intermediates rather than dissociating to separate reactive groups are termed vitrimers. Vitrimers were postulated to be an attractive subset of CANs, because associative cross-link exchange mechanisms maintain the original cross-link density of the network throughout the exchange process. As a result, associative CANs demonstrate a gradual, Arrhenius-like reduction in viscosity at elevated temperatures while maintaining mechanical integrity. In contrast, CANs reprocessed by dissociation and reformation of cross-links have been postulated to exhibit a more rapid decrease in viscosity with increasing temperature. Here, we survey the stress relaxation behavior of all dissociative CANs for which variable temperature stress relaxation or viscosity data are reported to date. All exhibit an Arrhenius relationship between temperature and viscosity, as only a small percentage of the cross-links are broken instantaneously under typical reprocessing conditions. As such, dissociative and associative CANs show nearly identical reprocessing behavior over broad temperature ranges typically used for reprocessing. Given that the term vitrimer was coined to highlight an Arrhenius relationship between viscosity and temperature, in analogy to vitreous glasses, we discourage its continued use to describe associative CANs. The realization that the cross-link exchange mechanism does not greatly influence the practical reprocessing behavior of most CANs suggests that exchange chemistries can be considered with fewer constraints, focusing instead on their activation parameters, synthetic convenience, and application-specific considerations.

Covalent Adaptable Network Reprocessing



Effect of
Mechanism?
Dissociative
vs
Associative

★ Both: Viscosity follows Arrhenius Relationship

INTRODUCTION

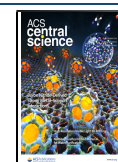
More than a century ago, Leo Baekeland patented the first fully synthetic polymer, a cross-linked phenolic resin that was later named Bakelite.¹ Unlike plastics that flow when heated, known as thermoplastics, Bakelite does not flow at elevated temperatures and is therefore classified as a thermoset. Owing to their cross-linked structures, thermosets possess exceptional physical properties, including high strength and modulus, making them excellent materials for coatings, composites, and adhesives. Although their permanent cross-links confer these desirable properties, they also preclude repairing, reshaping, or reprocessing at elevated temperatures. As such, thermosets like Bakelite have traditionally been considered much more difficult to recycle and not able to be directly reprocessed.

As early as 1946, cross-linked polymers were reported to relax stress due to exchange reactions of the cross-links,^{2,3} and the rate of this process was noted to have an Arrhenius dependence on the temperature. In the case of vulcanized rubber, Tobolsky postulated that stress relaxation was due to disulfide exchange.^{4,5} Other early publications reported similar stress relaxation in polyurethanes⁶ and polysiloxanes.⁷ In the last 20 years, coinciding with increased interest in sustainability

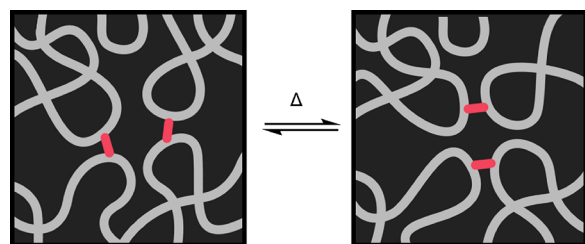
and stimuli-responsive polymers, dynamic reactions have been investigated to develop reprocessable cross-linked materials now known as covalent adaptable networks (CANs).⁸ Many of these materials behave like classic thermosets at room temperature but become malleable and reprocessable at elevated temperatures. Although room temperature creep in thermoset materials has historically been undesirable, cross-linked materials capable of thermally gated stress relaxation allows for reshaping and repair. The development of CANs shows promise for improving the lifetime and circularity of plastics, polymer self-healing, and applications ranging from healable polymer electrolytes for batteries^{9,10} to stimuli-responsive biomaterials¹¹ (Figure 1). These diverse applications invite a broad range of chemistries and a rigorous

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understanding of the necessary design constraints of these systems.



Dynamic Crosslink Exchange

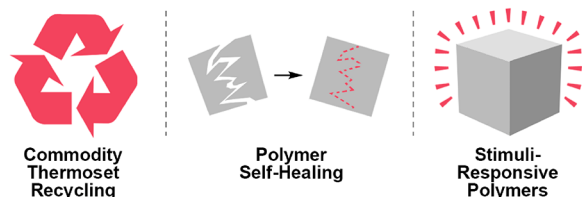


Figure 1. Depiction of stress relaxation in CANs, which imparts dynamic processes and functions into cross-linked polymers.

Thermally activated CANs are currently divided into two categories based on their cross-link exchange mechanism: (1) dissociative or reversible addition CANs, in which bond breaking precedes bond reformation, analogous to the S_N1 reaction, and (2) associative or reversible exchange CANs, in which new bond formation precedes bond breaking, analogous to the S_N2 reaction (Figure 2).^{12,13} It should be noted that in many cases, such as for disulfides, the molecular exchange mechanism may be ambiguous or condition-dependent.¹⁴ A classic, unambiguous example of a dissociative CAN is a network cross-linked by Diels–Alder (DA) adducts (Figure 2A).^{15,16} Upon heating, the rate of the retro-DA reaction increases with respect to the forward-DA reaction, which first leads to network rearrangement and can eventually induce a gel-to-sol transition.¹⁷ In 2011, Leibler and co-workers reported a prototypical associative CAN, a cross-linked polyester that was thermally reprocessed via transesterification (Figure 2B).^{18,19} In these systems, the rate of cross-link exchange also increases as a function of temperature. However, the total number of cross-links remains constant, such that the

network does not depolymerize as it is heated. Notably, unlike thermoplastics, whose viscosity decreases rapidly around T_g , the viscosity of this network followed an Arrhenius relationship, behaving like vitreous silica and other strong glass formers. Accordingly, CANs with associative cross-link exchange reactions were termed “vitrimers.”²⁰ Since the vitrimer concept was articulated, much attention has been focused on identifying other associative cross-link exchange chemistries, in part motivated by the hypothesis that vitrimers will exhibit unique characteristics relative to dissociative CANs under common reprocessing conditions.²¹

The differences in the thermal behavior between vitrimers and thermoplastics are apparent in an Angell fragility plot, which relates viscosity and temperature (Figure 3). Whereas

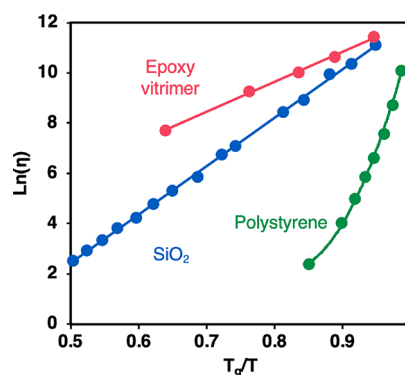
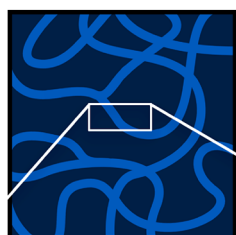


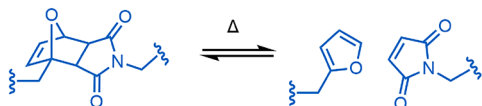
Figure 3. An Angell fragility plot comparing the evolution of viscosity above T_g for vitreous silica (blue),²⁸ an epoxy vitrimer (red),²⁹ and linear molecular weight = 3400 Da polystyrene (green).³⁰

the viscosity of linear polystyrene drops abruptly when heated above its glass transition temperature (T_g), both silica and vitrimers show a slow, linear decrease in viscosity (η). It has been asserted that dissociative CANs behave like thermoplastics in that they should evolve from a solid-like to liquid-like state more abruptly, as described by the Williams–Landel–Ferry model (WLF).^{22,23} The distinction between exchange mechanisms has strongly influenced the classification of CANs as well as the design and discussion of newly reported systems. More recently, it has been noted that dissociative CANs that undergo cross-link exchange with low degrees of de-cross-linking undergo stress relaxation and reprocessing that are virtually indistinguishable from those of true vitrimers.^{12,21}

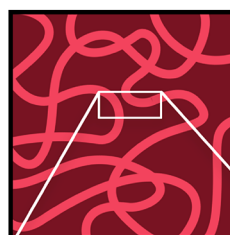
A. Dissociative CANs



- Bond dissociation precedes bond reformation
- Loss of crosslink density upon heating



B. Associative CANs (Vitrimer)



- Bond formation precedes bond dissociation
- Maintain crosslinking density upon heating

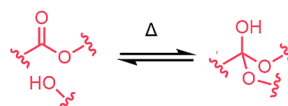


Figure 2. Depiction of cross-link exchange mechanisms in representative dissociative and associative CANs.

Indeed, several examples of dissociative CANs that demonstrate Arrhenius behavior over their reprocessing temperatures have been described as “vitriimer-like”^{24–27} or erroneously classified as vitrimers. Indeed, the subtle or nonexistent differences in properties between dissociative CANs and vitrimers casts doubt on the value of classifying these materials on the basis of the cross-link exchange mechanism.

In this Outlook, we examine all dissociative CANs for which stress relaxation or viscosity measurements have been reported as a function of temperature. Our survey reveals that dissociative CANs that have been characterized in this way exhibit thermomechanical characteristics similar to the vitrimers. All of these dissociative CANs exhibit Arrhenius-like relationships between temperature and stress relaxation or viscosity. While previous reviews have noted this behavior for specific dissociative CANs,^{12,21,31} here, we demonstrate that it holds true for dissociative CANs in general. In fact, there is little evidence that associative and dissociative CANs have significantly different behavior within typical reprocessing temperature ranges (typically 100–200 °C). Given the term vitriimer was coined to highlight the Arrhenius relationship demonstrated by associative CANs, yet this relationship is observed for all CANs, in this Outlook, we argue against further use of the term vitriimer. Additionally, we suggest that dissociative CANs with high thermal stability might prove even more versatile than vitrimers by accessing two different reprocessing regimes: the first, Arrhenius-like to enable reshaping and repair, followed by a second, low-viscosity regime that could facilitate certain melt processing methods. Ultimately, the practical differences between associative and dissociative CANs at typical reprocessing temperatures are relatively subtle. Where deviation is observed typically occurs at high temperatures. This understanding will greatly broaden the design space available to CANs, especially as they impact promising areas, including improving thermoset sustainability, polymer compatibilization, stimuli-responsive systems, and others.

Ultimately, the practical differences between associative and dissociative CANs at typical reprocessing temperatures are relatively subtle.

■ CHARACTERISTICS OF VITRIMERS

A vitriimer is a CAN whose long-term stress relaxation at elevated temperatures is enabled by an associative exchange reaction. As a result of this mechanism, vitrimers show constant cross-link density upon heating and an Arrhenius dependence of viscosity on temperature.^{20–22} Many approaches may be employed to probe the mechanism of bond exchange in a CAN, including experiments with well-defined model compounds. The relevant thermomechanical properties are typically studied via dynamic mechanical thermal analysis (DMTA) and stress relaxation analysis (SRA). An illustrative example comes from Du Prez and co-workers' work on vinyllogous urethane vitrimers, which contain free amine groups thought to engage in associative bond exchange (Figure 4A).³²

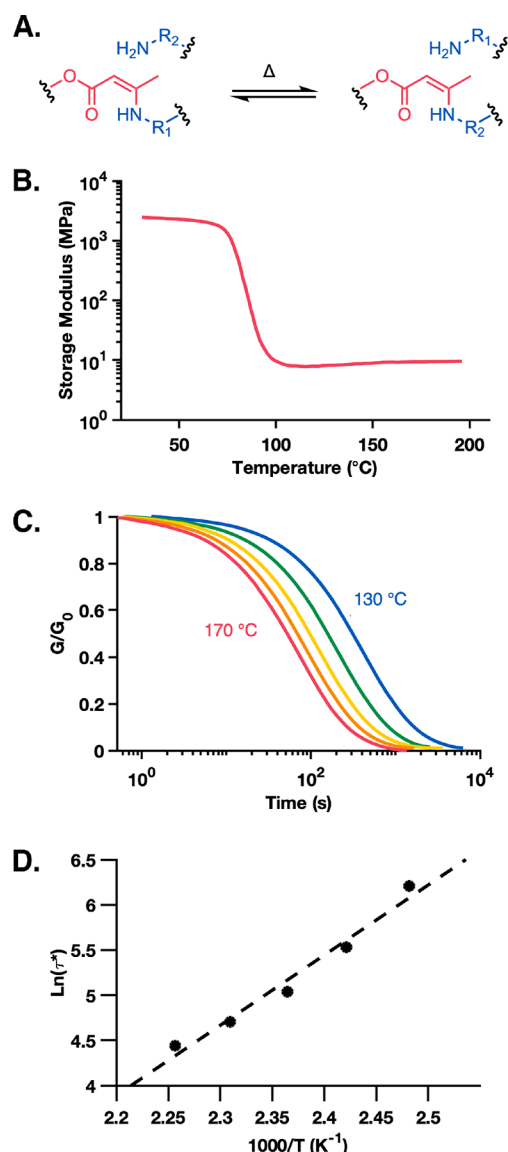


Figure 4. (A) Structure of cross-linked vinyllogous urethanes that relax stress through an associative reaction and demonstrate the characteristic properties of vitriimer. (B) A DMTA trace exhibits a constant storage modulus above T_g . (C) Normalized stress relaxation analysis at temperatures between 130 and 170 °C. (D) Arrhenius plot of the characteristic relaxation time (τ^*) against inverse temperature.

According to DMTA plots, for these polymers above the glass transition temperature, the storage modulus remains constant up to at least 200 °C (Figure 4B). For incompressible materials with a Poisson's ratio close to 0.5, the elastic modulus (E') above T_g may be used to estimate the molar mass between cross-links (M_c) via the equation

$$M_c = \frac{3\rho RT}{E'} \quad (1)$$

where ρ is the density of the material, R is the gas constant, and T is the absolute temperature.³³ As suggested by eq 1, assuming constant density, the presence of a constant modulus above T_g suggests the molecular weight between cross-links remains constant upon heating. Although thermoplastic melts sometimes also show a plateau in the DMTA ascribed to chain entanglement, a rubbery plateau that persists for more than 100 °C is indicative of a cross-linked material.

Table 1. Summary of Reported Vitrimers, Listing the Type of Associative Chemistry, the Catalyst (If Used), the Temperature Range for SRA, and the Calculated E_a of Viscous Flow

associative exchange chemistry	catalyst	temperature range (°C)	E_a (kJ mol ⁻¹)	reference
transesterification	Zn(OAc) ₂	100–280	88	19
	benzenesulfonic acid	25–75	56	38
transcarbamoylation	—	170–190	111	32
transcarbonation	Ti(OiPr) ₄	150–180	111	39
vinylogous urethane transamination	—	130–170	60	40
	—	80–160	81	41
	—	135–150	102	42
	—	190–220	75	43
	—	135–150	123	44
vinylogous urea transamination	—	140–170	44	45
	pTsOH	140–170	45	45
diketoenamine transamination	—	140–170	49	46
transimination	—	50–127.5	157	47
transalkylation of trialkylsulfonium salts	—	120–150	108	48
transthioetherification	—	120–150	63	49
olefin metathesis	Grubbs second gen catalyst	15–30	96	50
dioxaborolane metathesis	—	130–160	77	51
silyl ether exchange	—	150–180	81	52

When viscosity shows Arrhenius-type behavior, it may be described using the following equation

$$\eta = Ae^{E_a/RT} \quad (2)$$

where A is a pre-exponential constant, and E_a is the activation energy for viscous flow.³⁴ For CANs above T_g , where flow is limited by the bond exchange, the primary contribution to E_a is the activation energy required for the bond exchange reaction.³⁵ However, the activation energy of viscous flow may be affected by many properties of the network, including polymer identity, topology, and cross-link density.³¹ As such, CANs with identical exchange chemistries may demonstrate varied values of E_a .³⁶

Typically, viscosity is probed indirectly by performing stress relaxation experiments, in which a sample is strained to a fixed length at constant temperature, and the change in relaxation modulus is measured over time (Figure 4C). The characteristic relaxation time τ^* is the time at which the stress relaxation modulus has decreased to 37% (1/e) of the initial value and may be related to viscosity via the following equation³⁷

$$\eta = \frac{1}{3}E'\tau^* \quad (3)$$

If E' is unchanging with temperature, $\ln(\tau^*)$ may be directly plotted against the inverse of the temperature (T) to give a line whose slope is proportional to E_a (Figure 4D). In this example, τ^* was plotted against $1000/T$, to provide an E_a of 60 kJ mol⁻¹. However, if the storage modulus (E') is not constant with increasing temperature, τ^* and E' may be used to calculate η at a given temperature.

The observation of an Arrhenius dependence has been one of the primary features used to characterize a CAN as a vitrimer, with the assumption that dissociative CANs behave differently. Table 1 includes these findings from a number of publications on associative CANs. The type of associative exchange chemistry in the network, the catalyst used, the temperature range for SRA, and the E_a , calculated from the Arrhenius plot, have been included. While other parameters (such as τ^* and $\ln \tau_0$) are important for understanding the behavior of these materials, they have not been included due to

inconsistent reporting. While the exact ranges vary, SRA is typically performed at temperatures around 150 °C. Bulk reprocessing is also commonly performed near this temperature.

■ DISSOCIATIVE CANS ALSO EXHIBIT ARRHENIUS RELATIONSHIPS BETWEEN VISCOSITY AND TEMPERATURE

Observing a constant modulus by DMTA and an Arrhenius viscosity relationship in SRA have been traditionally used to classify a CAN as a vitrimer, but these features are also regularly observed in dissociative CANs. Although dissociative reactions do reduce the cross-link density during reprocessing, in most systems, it is clear that only a small degree of cross-link reversion occurs under the reprocessing conditions. This situation results in stress relaxation behavior that remains limited by bond exchange and therefore also follows an Arrhenius relationship. Many DMTA experiments performed on dissociative CANs show rubbery plateaus over a broad range of elevated temperatures. This plateau, as measured from T_g to the gel-to-sol transition temperature, often extends for at least 60 °C and persisted for 120 °C in a system based on hindered urea exchange reported by Rowan and co-workers.²⁴ For CANs with high thermal stability, the modulus eventually drops above a gel-to-sol transition temperature, at which point enough cross-links have dissociated to enable flow similar to thermoplastics.^{53–55}

CANs based on polyurethanes are prototypical materials that undergo dissociative exchange, reprocess similarly to vitrimers over a broad temperature range and depolymerize further at still higher temperatures. In the presence of a transition metal catalyst at elevated temperatures, the urethanes partially revert into alcohols and isocyanates, as demonstrated by small molecule studies (Figure 5A).⁵⁶ Nevertheless, these cross-linked materials display the properties typical of vitrimers. A DMTA trace, collected to elevated temperatures for this Outlook, reveals a rubbery plateau of constant modulus between 80 and 160 °C (Figure 5B). While enough urethane exchange occurs in this temperature range to observe stress relaxation on the order of tens of seconds,

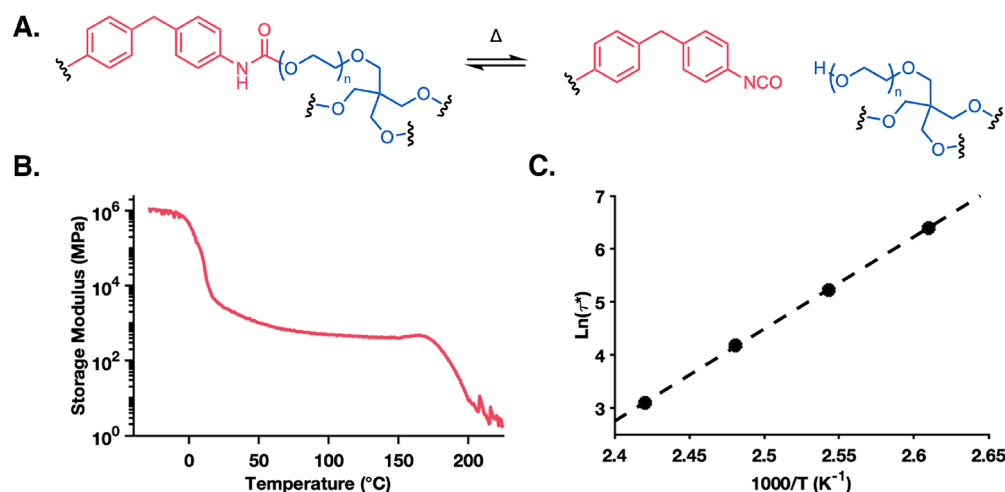


Figure 5. (A) Structure of polyurethane that relaxes stress through a dissociative mechanism but demonstrates the properties of vitrimers. (B) A DMTA trace shows a plateau in storage modulus above T_g , then a decrease associated with depolymerization. (C) Arrhenius plot of $\ln(\tau^*)$ against inverse temperature.

Table 2. Summary of Previously Reported Dissociative CANs, Listing the Type of Associative Chemistry, the Catalyst or Additive If Used, the Temperature Range for SRA, and the Calculated E_a of Viscous Flow

dissociative exchange chemistry	catalyst/additives	temperature range (°C)	E_a (kJ mol ⁻¹)	reference
retro-Diels–Alder	4-dimethylaminopyridine	60–110	40	16
	—	100–140	95	57
	—	60–90	114	58
urethane dissociation	—	80–130	108	27
	dibutyltin dilaurate	110–140	144	56
urea dissociation	—	50–120	59	24
	—	90–190	130	24
alkyl urea dissociation	—	80–170	109	59
anhydride formation	—	100–180	120	60
homolytic C–C bond cleavage	—	125–175	84	61
	—	70–120	103	62
triazolinedione reversibility	ZrAc ₄	120–150	108	63
transalkylation	—	130–200	140	64
	—	130–180	150	65
transamidation	—	110–160	91	66
transamination	—	50–75	52	67

network integrity is maintained. When SRA was performed between 110 and 140 °C, the values of τ^* obeyed the Arrhenius relationship (Figure 5C). However, unlike with associative CANs, when the temperature exceeds 180 °C, the cross-link density decreases precipitously. This second thermal transition will only be observed in materials with sufficient thermal stability and is often not investigated. It can in principle be observed for any dissociative equilibrium, as the entropic benefit of bond breaking will dominate at sufficiently high temperatures.

The above example is not aberrant. Every dissociative CAN for which SRA measurements were reported at multiple temperatures demonstrated the Arrhenius relationship typically associated with vitrimers.^{16,24,27,56–58,60–67} Table 2 summarizes these findings, including the type of dissociative exchange chemistry, catalyst if used, the temperature range for SRA, and the E_a , calculated from the Arrhenius plot. Notably, both the temperature at which these experiments were performed and the calculated E_a values were in a similar range to those of associative CANs.

Every dissociative CAN for which SRA measurements were reported at multiple temperatures demonstrated the Arrhenius relationship typically associated with vitrimers.

It should be noted that not all dissociative CANs display a constant modulus above their T_g .^{68–70} However, even this feature does not preclude the dissociative CANs from showing an Arrhenius relationship in their stress relaxation. Xie and co-workers reported a DA-cross-linked network (Figure 6A) that shows a DMTA trace in which the modulus continuously decreases above its T_g (Figure 6B).⁵⁸ However, after we calculated the viscosity using the reported τ^* values and the storage modulus from the DMTA data, we observed that the viscosity nevertheless shows an Arrhenius relationship with temperature (Figure 6C). This example highlights both the prevalence of this Arrhenius relationship in dissociative CANs

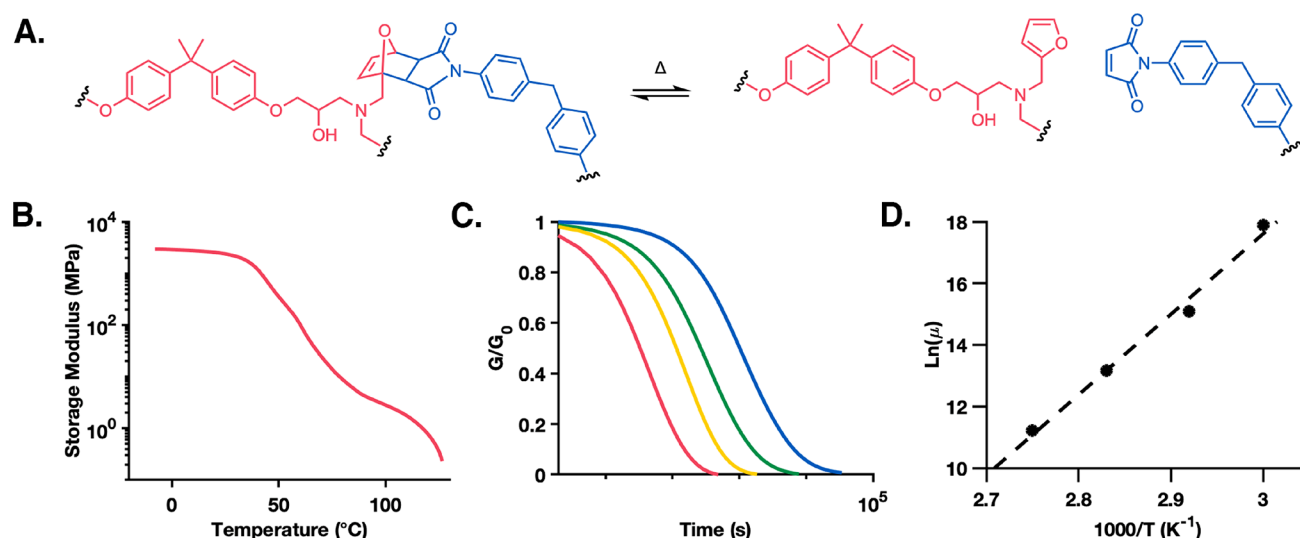


Figure 6. (A) Structure of a cross-linked polymer containing Diels–Alder adducts. (B) A DMTA trace shows a continually decreasing storage modulus. (C) Normalized stress relaxation analysis. (D) An Arrhenius plot of $\ln(\eta^*)$ against inverse temperature.

and the need to perform SRA over a wide range of temperatures to fully understand the thermal properties of CANs.

MERITS OF ASSOCIATIVE AND DISSOCIATIVE CANs

Both associative and dissociative CANs show an Arrhenius relationship as a result of exchange reactions limiting polymer flow. As such, the term vitrimer is of questionable value as a classification, as it implies that materials differ strongly in how their viscosities evolve with temperature as a function of their cross-link exchange mechanisms. Given the similarity between their thermal properties under typical reprocessing conditions, it is important to examine relative advantages and disadvantages of associative and dissociative CANs with more nuance. Dissociative CANs show an Arrhenius dependence in a certain temperature range, eventually undergoing dissolution above a gel-to-sol temperature. At high-enough temperatures, assuming no irreversible side reactions, dissociative CANs may be melted and reformed as the temperature is lowered. As a result, certain dissociative systems might prove compatible with a broader range of reprocessing methods that rely on accessing lower viscosity.

One should also acknowledge that the rate laws for associative and dissociative reactions will differ. For example, the rate of transesterification reaction will be accelerated by increasing the concentration of free hydroxyl groups in the network. In addition, consider a dissociative CAN with cross-links formed from the Diels–Alder reaction between a furan and a maleimide. Increasing the concentration of free furan or maleimide would enhance the rate of cross-link reformation at elevated temperatures. Certainly, understanding the reaction mechanism may facilitate the design and optimization of CAN networks. However, given that many factors may influence the performance and properties of both associative and dissociative CANs (including catalyst concentration, identify of backbone polymer and reactive groups, among others), neither type of CAN inherently gives the researcher more tunable design parameters.

Another hypothesized distinction between associative and dissociative CANs is that associative networks, by maintaining

constant cross-linking density, will show superior resistance to nonreactive solvents. Dissociative systems, on the other hand, are likely to dissolve as bonds broken in the solid state are unlikely to reform as the network swells and loses integrity. Certain vitrimers have shown evidence of excellent solvent resistance, but this behavior has not been investigated fully. Although not yet demonstrated experimentally, associative networks can in principle dissolve in nonreactive solvents by forming loops that separate one portion of the network from another. The effect of loops in polymer networks remains of considerable interest.^{71–73} The rates of dissolution between associative and dissociative CANs might vary dramatically, such that it is reasonable to expect vitrimer dissolution to occur more slowly. Further studies are necessary to probe these effects.

While researchers continue to investigate CANs, moving away from the rigidly defining them based on their exchange mechanisms removes unneeded constraints on their design. As the field of CANs has matured, there is now the potential to use this chemistry for polymer recycling⁴⁶ and even plastic upcycling⁷⁴ and compatibilization,⁷⁵ conductive polymers,^{76–78} solid-state electrolytes,^{9,10} and biomaterials,¹¹ and perhaps many other uses. The successful implementation of CANs for these applications will benefit from a broad range of accessible chemistries, and in most cases, these systems may be designed without regard to whether cross-link exchange mechanisms are associative or dissociative. Given potential issues of compatibility of functional groups in a material, the fact that a range of chemistries demonstrate similar thermomechanical properties, regardless of the mechanism of exchange, allows researchers to choose from a greater pool of potential exchange chemistries.

Our analysis is limited to work where multiple SRA experiments were performed at varying temperatures. However, many studies of dissociative CANs do not investigate the stress relaxation of the materials, and therefore, these studies are not included in our analysis. However, none of these studies give additional indications that the CANs are likely to behave differently than those profiled here. Also, some reports perform stress relaxation studies only over a limited temperature range. Although these ranges are sufficient to demonstrate an Arrhenius relationship, larger temperature

ranges should be investigated, especially when looking to probe how the material's thermal behavior deviates from linearity as it approaches the gel-to-sol transition temperature. Likewise, when acquiring DMTA data, we recommend performing experiments to higher temperatures to potentially observe a gel-to-sol transition. Additionally, thermogravimetric analysis is necessary to understand the decomposition of these materials, typically observed above 200 °C.

It should also be noted that in most publications, an Arrhenius relationship was shown by plotting $\ln(\tau^*)$ against the inverse temperature. However, in order to find τ^* by using the time at 37% of initial modulus from SRA, stress relaxation must fit a single Maxwell model. Given that networks dissipate stress through many relaxation modes, researchers might instead consider fitting these SRA traces with more sophisticated models, such as the Kohlrausch–William–Watts model.⁷⁹ Additionally, other experiments and analyses, including creep tests and the use of time–temperature superposition, give additional insight into the behavior of these materials.

CONCLUSIONS

The full potential of CANs will certainly involve a deep understanding of their physical organic chemistry and design constraints. The expansion of this field over the past decade has provided many CANs with diverse chemistries, which now allow a re-evaluation of the relative merits of associative and dissociative cross-link exchange mechanisms. Under the typical temperature ranges used for material reprocessing, dissociative CANs do not demonstrate markedly different thermal properties from associative networks. When the appropriate experiments are performed, dissociative CANs show the Arrhenius behavior commonly believed to be indicative of vitrimers. Therefore, reserving the term vitrimer, which refers to the glass-like thermal properties of these materials, to only associative CANs is misleading and overly restrictive. While understanding the bond exchange mechanism is undoubtedly important for the design and understanding of new dynamic materials, properties including T_g , E_a , the gel-to-sol and degradation temperatures, and the identity of reactive groups are more important when selecting appropriate exchange chemistries. Further research is needed to explore the unique properties of dissociative CANs, especially for networks with sufficient thermal stability to access non-Arrhenius behavior near their gel-to-sol transition temperature. Importantly, we believe that the similarity of CAN behavior under typical reprocessing conditions liberates the design constraints on these materials and should encourage research into new exchange chemistries that do not fit the rigid definition of vitrimers.

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Notes

The authors declare no competing financial interest.

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