HAL
open science

Neighboring Group Participation and internal catalysis effects on exchangeable covalent bonds: Application to the thriving field of vitrimers chemistry

Florian Cuminet, Sylvain Caillol, Éric Dantras, Eric Leclerc, Vincent Ladmiral

To cite this version:

Florian Cuminet, Sylvain Caillol, Éric Dantras, Eric Leclerc, Vincent Ladmiral. Neighboring Group Participation and internal catalysis effects on exchangeable covalent bonds: Application to the thriving field of vitrimers chemistry. Macromolecules, 2021, 54 (9), pp.3927-3961. 10.1021/acs.macromol.0c02706 . hal-03224634

HAL Id: hal-03224634

https://hal.science/hal-03224634v1

Submitted on 11 May 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Neighboring Group Participation and internal catalysis effects on exchangeable covalent bonds: Application to the thriving field of vitrimers chemistry

Florian Cuminet,[1] Sylvain Caillol,[1] Éric Dantras,[2] Éric Leclerc,[1] Vincent Ladmiral[1]*

[1]ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France
[2]CIRIMAT, Université de Toulouse, Physique des Polymères, 118 Route de Narbonne, 31062 Toulouse, France
*Corresponding author: Vincent Ladmiral, Email: vincent.ladmiral@enscm.fr

Abstract

Vitrimers constitute a fascinating class of polymer materials which make the link between the historically opposed 3D networks (thermosets) and linear polymers (thermoplastics). Their chemical resistance, reshaping ability and unique rheological behavior upon heating make them promising for future applications in industry. However many vitrimers require the use of high catalyst loadings, which raises concerns for their durability, and limits their potential applications. To cope with this issue, internal catalysis and neighboring group participation (NGP) can be used to enhance the reshaping ability of such materials. A few studies report the effect of activating groups on the exchange reactions in vitrimers. Nevertheless, knowledge on this topic remains scarce, although research on vitrimers would greatly benefit from NGP already known in organic chemistry. The present perspective article presents the different types of exchangeable bonds implemented in vitrimers and discusses chemical groups known to have or potentially capable of an enhancing effect on exchange reactions. This analysis is underpinned by a thorough mechanistic discussion of the various exchangeable bonds presented.

(I) Introduction

Since the team of L. Leibler discovered and described the first vitrimer in 2011,[1] these materials have attracted tremendous attention in the polymer and materials communities. This enthusiasm is not surprising given the amazing properties of these materials. Nevertheless, though the definition of this concept seems easy to handle at first glance, caution should be taken when classifying new materials as vitrimers. To understand well what a vitrimer is, the usual classification of polymer materials must be clearly reminded. Historically, polymers have been categorized in two main classes: thermoplastics and thermosets. Thermoplastics consist of entangled linear polymer chains which are free one from another. In contrast, in thermosets, polymer chains are linked by covalent bonds which cannot be cleaved without destroying the network.[2] This difference at the molecular scale has consequences on the macroscopical behaviour of these materials. Most thermoplastics are soluble provided that a convenient solvent is used (or exists). In thermosets the solvent is not able to set the chains apart, and the material does not dissolve. Besides this different behaviour towards solvents, the other main difference lies in the thermal behaviour of these materials. In most cases when thermoplastics are heated, the relative movement of the chains becomes easier. Macroscopically this phenomenon is visible when the material flows.[2] Thermosets cannot flow when heated.[2,3]

Reversible reactions involving covalent bonds have been known for many decades, and their possible use in polymers had already been inferred in the 1960s.[4,5] The concept of reversible covalent

bonds implemented in polymers led to a new class of materials called CANs, short for covalent adaptable networks. In CANs, polymer chains are covalently crosslinked as in thermosets, but these crosslinking bonds are reversibly cleavable, which leads to properties such as malleability in response to an external stimulus such as temperature or light irradiation.[6] The most iconic reversible reaction used in such materials is probably the Diels-Alder reaction.[7–13] This reaction is reversible upon heating. When this reaction is used to make crosslinked materials, the crosslinking bonds can break upon heating and reform at lower temperature, thus leading to reshapability (Figure 1C).[6] Most CANs designed before the year 2010 were based on dissociative mechanism whereby a bond has to be cleaved before another bond is formed between the dissociated moieties.

In 2005, Bowman et al. reported the first CAN based on an associative exchange reaction.[14] Allyl sulphides were used as addition-fragmentation chain transfer agents. The exchange proceeded via a photo-induced radical mechanism allowing constant crosslinking density and network connectivity even though the topology changed.[14]

Later, in 2011, Leibler et al.[1] described the first thermally-triggered associative CAN, based on transesterification as the exchange reaction. This material exhibited a novel rheological behaviour with its viscosity decreasing linearly with increasing temperature. Because this behaviour is common in inorganic materials and especially strong glass, this new kind of polymers was coined “vitrimer”. On the one hand, vitrimers are often insoluble like thermosets, except for specific cases such as very fast vitrimers for instance.[15,16] On the other hand, they can be reshaped and recycled by heating without precise control over temperature, like glass. Their singular rheological behaviour was attributed to the associative mechanism of the bond exchange. In contrast to the majority of dissociative CANs, because vitrimers keep a constant connectivity regardless of the temperature (even the reshaping temperatures), their viscosity only depends on the rate of the exchange reaction. Therefore, the viscosity and stress relaxation profiles as a function of temperature follow Arrhenius law. These behaviours are often considered specific to vitrimers,[1,17–19] although this point has recently been questioned, and is debatable.

Two visions of what a vitrimer is coexist, depending on whether the chemist’s or the physicist’s point of view is adopted. The chemist’s definition focuses on the exchange mechanism. In consequence, only a CAN based on an associative mechanism is a vitrimer (Figure 1A). In contrast, the physicist defines a vitrimer according to the physical properties. For example, Drockenmuller et al.[20] described a material based on a dissociative mechanism which exhibits an Arrhenius viscosity dependence with temperature. Such materials were designated as “vitrimer-like”.[21] The hypothesis to explain such vitrimer-like behaviour in dissociative CANs lies in the thermodynamic and kinetic of the exchanges. When the equilibrium constant of dissociative bonds is displaced towards the associated state, though the dissociation-association happens, the overall number of bonds and crosslink density is barely reduced. Kinetically, this happens when the association reaction is much faster than the dissociation reaction. The dissociated state is thus transitory, globally the number of bonds hardly changes and the network integrity remains virtually unchanged (Figure 1B).[22,23] The Arrhenian rheological behaviour can also be observed in a range of temperatures over which the equilibrium constant does not vary much. For instance, Konkolewicz et al. made vitrimer-like dissociative CANs out of anilinium salts. They reported for the adduct formation a ΔH value of -2.8 ± 0.2 kJ mol^{-1}, and compared it with the case of Diels-Alder adduct formation with ΔH value of -157 ± 14 kJ mol^{-1}.[21] Because ΔH is very low for their system, the dependence of K_{eq} with temperature is considered negligible. In this case, the ratio of dissociated and associated bonds over this temperature range is constant (Figure 1B) and the network connectivity does not change.[21,24] With the increasing number of chemical platforms able to undergo exchange discovered, some particular cases of dissociative

CANs somewhat blur the boundary with vitrimers.[20,21,25,26] In addition, networks featuring both permanent and exchangeable crosslinks are reported to exhibit vitrimer-like stress-relaxation, but within a certain limit as the permanent crosslinks induced a residual stress plateau.[27] Such borderline materials indicate that the definition of a vitrimer still remains debatable, depending on the viewpoint adopted.

Vitrimers address the problem of thermoset recyclability and thermoplastic vulnerability towards solvents. Therefore, the interest for these materials is growing in industry, as highlighted in recent reviews.[22,28,29] Nonetheless some characteristics may limit their industrialization. They often display high relaxation times and high viscosity during reprocessing, making them unsuitable for the recycling processes usually found for thermoplastics in industry. Furthermore, most vitrimers rely on catalysts and in some cases on high catalyst loadings.[1] The use of catalysts may generate problems such as limited number of recycling/reshaping cycles due to premature degradation, or migration and loss of the catalyst.[30–32] A solution to this issue is the design of vitrimers that do not rely on catalysis. This can be done by using a large excess of exchanging functional groups[32–34] or by using exchange reactions which do not require any catalyst.[18,35-42] Another strategy, inspired by organic chemistry in solutions, relies on chemical functions near the exchangeable bond to enhance the reaction rate. This effect is called either neighboring group participation (NGP) when the accelerating substituents are at some point covalently bonded to the reaction center during the exchange, or internal catalysis for effects at longer distance such as electrostatic interactions, steric effects or weak bonds.[43] Guan et al.[44] implemented this strategy in boronic esters CANs and enhanced the transesterification rate thanks to neighboring tertiary amines. This effect was latter implemented in other kinds of vitrimers featuring ester or silyl ether exchangeable bonds for instance.[38,45] In their review, Guerre et al.[43] highlighted the few examples of internal catalysis in vitrimers reported so far, and the strong potential of this strategy to tune the properties of vitrimers. More recently, Van Lijsebetten et al.[46] also emphasized the power of NGP in dynamic covalent chemistry, especially in polymeric materials, in a very clear and useful tutorial review. To go further on this concept, a general outline of the activating groups potentially beneficial to vitrimers would give useful insight for further research on this fast rising topic. Nevertheless, caution should be taken when using NGP as this strategy can sometimes drastically modify the exchange mechanism.[24,43] For instance, transesterification which usually proceeds via an associative exchange, was reported to follow a dissociative pathway in the presence of specific activating groups.[47,48]

Activating groups are a very powerful yet complex tool. Because the case of vitrimer-like dissociative CANs is still debated in the vitrimer community, this Perspective article focuses on internal catalysis and NGP in associative exchange reactions, to follow the strict definition of vitrimers. The first part is dedicated to the description of the associative exchange reactions implemented in vitrimers, their mechanisms and some of the pitfalls a vitrimer scientist should be aware of (Figure 2). Then, in the light of this mechanistic discussion, the activating groups potentially useful to tune the properties of vitrimers are briefly presented and discussed. Insights on the activating groups proven to be beneficial on small molecules, but not yet implemented in vitrimers are also given. For each kind of exchangeable bonds the influence on the exchange reactions kinetics are discussed as well.

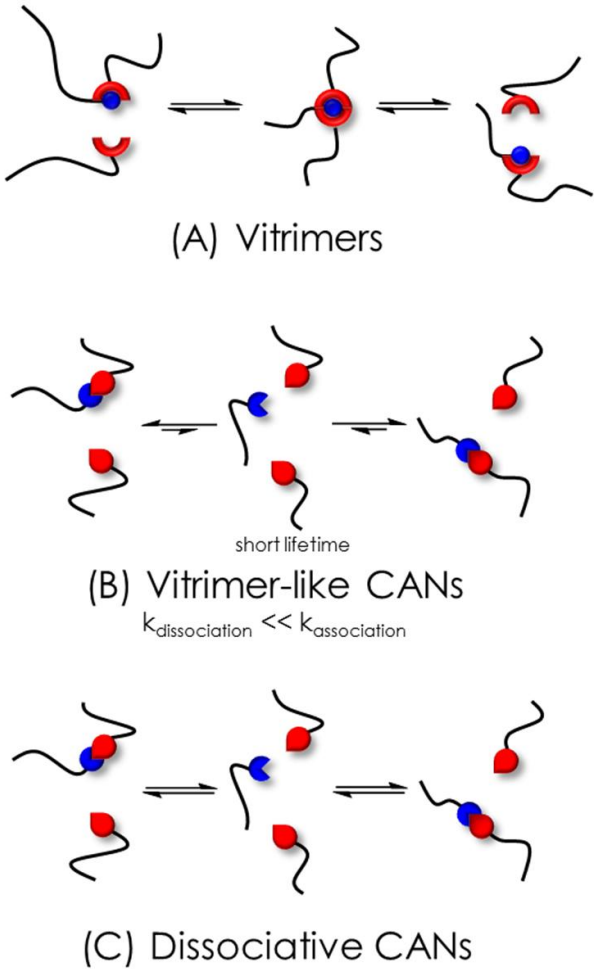


Figure 1. Schematic representations of the mechanisms at work in: A) associative CANs (vitrimers), B) Vitrimer-like dissociative CANS and C) dissociative CANs. Vitrimer-like dissociative CANs (B) exhibit a constant K_{eq} over the vitrimer-like temperature regime and a short lifetime of the dissociated state.

(II) Exchangeable bonds with an associative mechanism

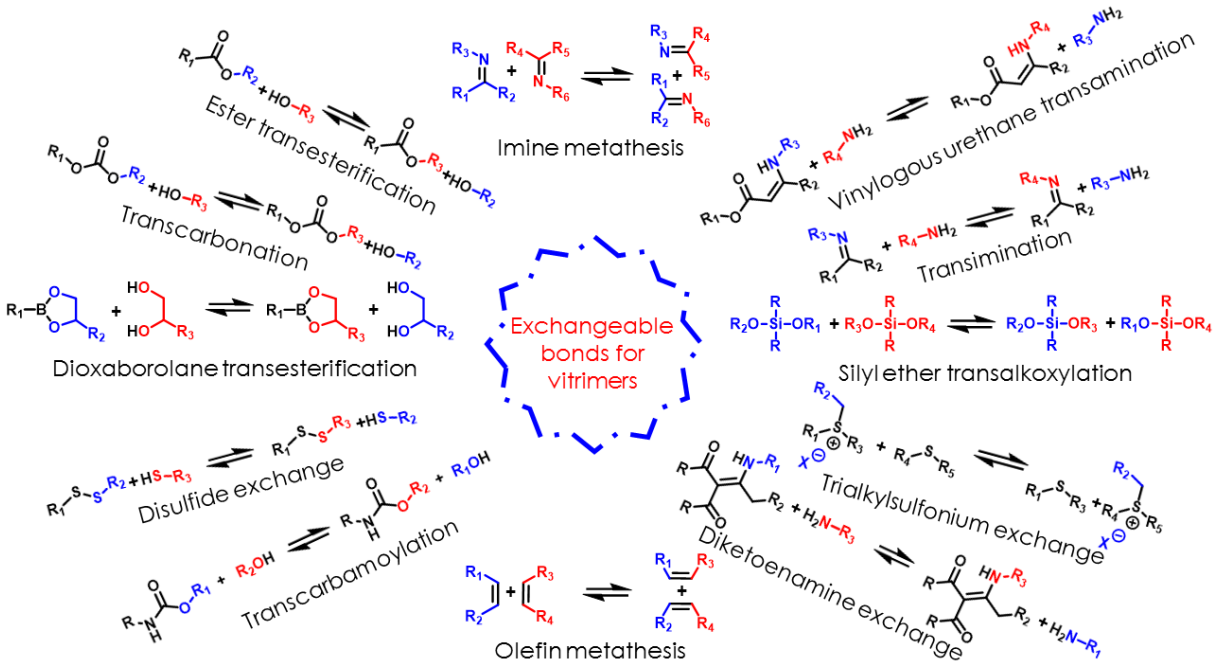
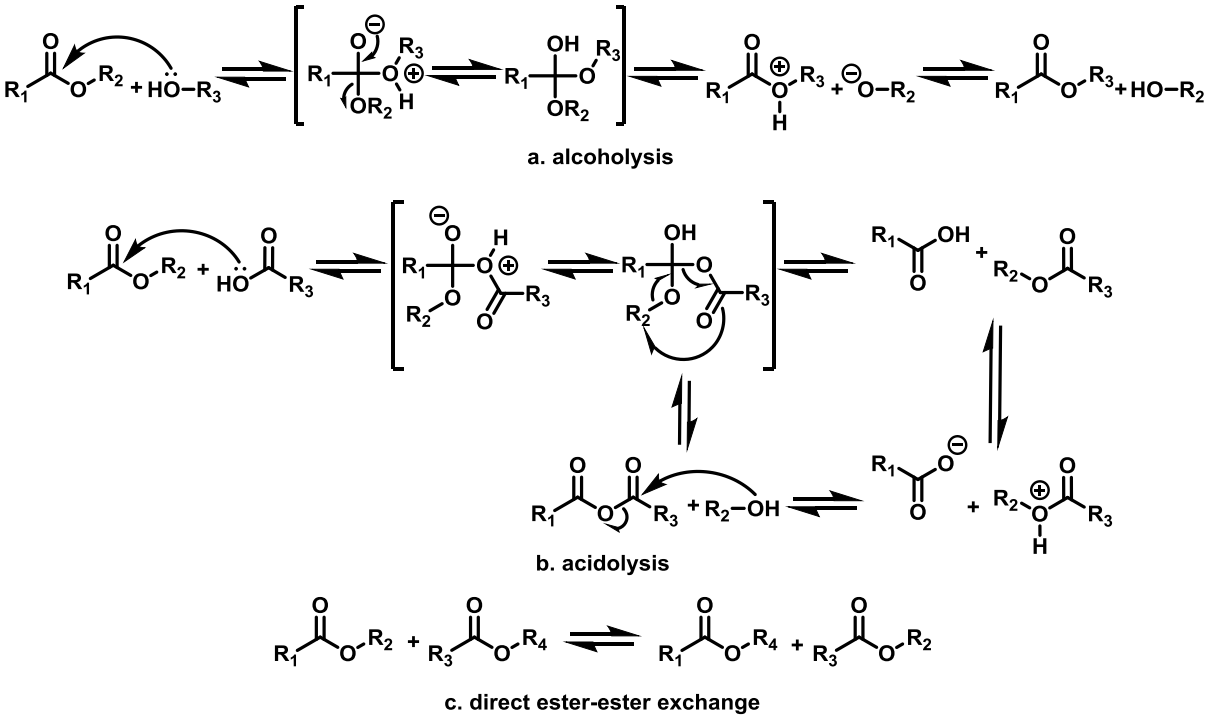


Figure 2. Associative exchangeable bonds for vitrimers design.

Esters

Esters are probably one of the oldest known exchangeable bonds, as Friedel and Craft, famous for the eponymous reaction, also discovered in 1865 the exchange reaction occurring between two ester groups.[49] Several terms such as ester exchange, ester-ester interchange, interesterification or the nowadays most commonly used transesterification are considered as synonymous, though they actually encompass several reactions.[50] Actually three reactions are reported to happen in what is commonly considered as the transesterification equilibrium,[51] namely alcoholysis, acidolysis and the genuine transesterification.[49,52–54] Alcoholysis is the main reaction[55] although the direct ester-ester exchange prevails for esters synthesized from aromatic acids over 300°C.[56] The alcoholysis mechanism proceeds by the attack of the alcohol onto the carbon of the carboxylate. A tetrahedral intermediate is thus formed prior to the elimination of an alkoxy group, leading either to the starting ester or to the exchanged one (Scheme 1a).



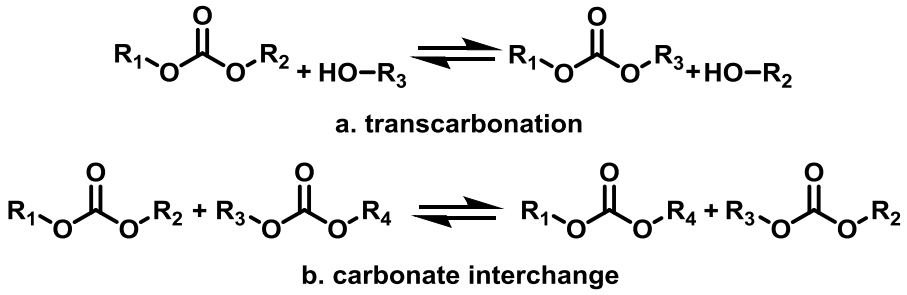
Scheme 1. Ester exchange mechanisms a. alcoholysis, b. acidolysis and c. direct ester-ester exchange.

The mechanism of acidolysis is similar: the nucleophilic oxygen of the acid attacks the electrophilic carbon of the carbonyl moiety of the ester and forms a tetrahedral intermediate, prior to the elimination of the attacking acid, or the exchanged one. Elimination of the alkoxy group on the intermediate can also occur. This produces an anhydride intermediate which reacts immediately with the released alcohol (Scheme 1b).[53,57] The third mechanism is less usual and is described as a concerted interchange (Scheme 1c). This reaction was reported experimentally thanks to kinetics experiment at temperatures over 300 °C.[56] Kotliar et al. pointed out that the enthalpy change during this reaction is near zero suggesting an associative pathway.[53] Anyway, these three mechanisms are associative. Catalysis does not seem to change this feature as acid-catalysed transesterification is reported to proceed through an addition/elimination mechanism.[58] Additionally, base catalysis only changes the nucleophile from an alcohol to its more reactive alkoxide counterpart.[59] Transesterification was studied in polymers in the second half of the twentieth century, as the exchange reaction is more significant in bulk materials,[49,52,55,60] then this reaction regained popularity

among scientists with the development of biodiesel and biofuels. Recently, the interest in biomass valorisation and greener fuels has grown and catalysts such as *N*-heterocyclic carbenes,[61] calcium oxide,[62] ZrO_2/SO_4,[59] silicates and clays[63,64] or aluminum chloride[65] were (re)discovered. Metal-based catalysis (such as Sn, Ti or Mg[51,54] for instance) draws particular attention as zinc-based catalysts were recently used in the first reported vitrimer.[1] The mechanism involves a Zn^{2+} species, which coordinates to the ester carbonyl group and activates it with respect to the nucleophilic attack of the alcohol or alkoxide, and then proceeds via the pathway previously described.[66] In summary, all the catalytic mechanisms encountered so far were associative.

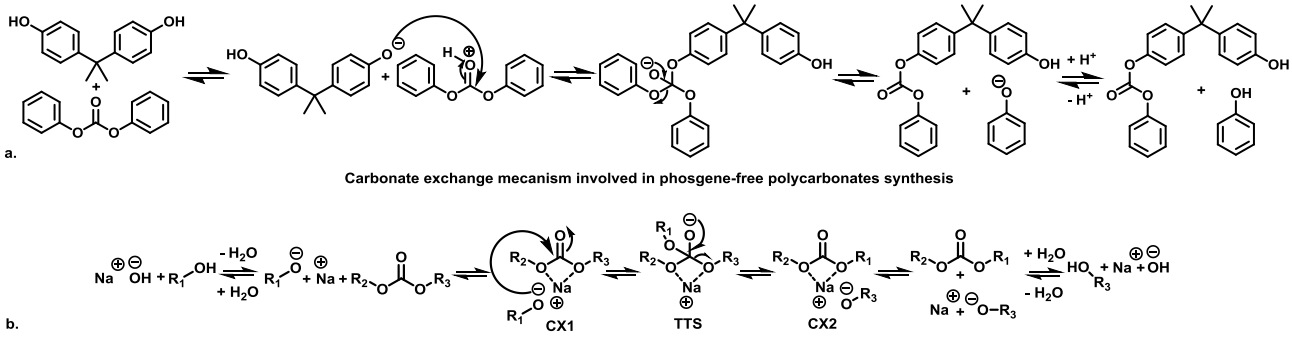
Carbonates

Owing to their structural similarity, carbonates and esters are often compared and their chemistries are considered very close. As in the case of esters, several names are used for the exchange reactions of carbonate. The exchange between an alcohol and a carbonate is called transcarbonation, carbonate transesterification or carbonate alcoholysis when the exchange occurs on polycarbonate chains and small alcohols (Scheme 2a). Carbonate interchange refers to the exchange between two carbonates (Scheme 2b).



Scheme 2. Exchange reactions on carbonates a. transcarbonation and b. carbonate interchange.

The interest for transcarbonation rose when scientists aimed at synthesizing polycarbonate materials without the use of highly toxic phosgene.[67] The exchange between diphenyl carbonate and bisphenol A was used as a safer pathway to produce polycarbonates. The mechanism involved was similar to ester transesterification[68] and was proven quite recently. In the absence of catalyst, there is a prototropy between the phenol and the carbonate. The deprotonated counterpart (phenolate) is the reactive species towards the electrophilic carbon of the carbonate carbonyl moiety. The reaction proceeds through a tetrahedral intermediate before the elimination of a phenolate (from the starting carbonate or from the reactant).[69,70] However, this exchange is very slow.[67] Transcarbonation is known to be catalyzed by metal-derived catalysts such as tin salts,[71-73] zinc acetate,[74] copper salts,[72] and even a dimetallic iron-manganese cyanide catalyst.[75] Bases are also common catalysts, for instance magnesium hydroxide,[76] calcium salts[77,78] or sodium alkoxides.[74,79] All the catalyzed mechanisms described are associative,[69,71,74,76-80] though they are slightly different depending on the type of catalysis employed (Scheme 3).



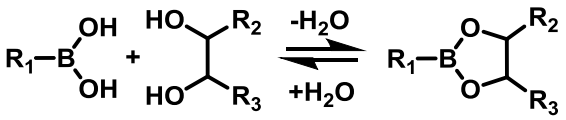
Scheme 3. a. transcarbonation pathway and b. catalytic effect by bases and metal ions.

When a base catalyst is used, the carbonate and the alcohol moiety are presumably hydrogen bonded in a pre-reaction complex (CX1). Then the reaction proceeds via a tetrahedral transition state (TTS) yielding a post-reaction complex (CX2) and ultimately the free exchanged species (Scheme 3b).[74] The overall reaction follows an "addition-elimination" mechanism. When a Lewis acid catalyst is employed, such as zinc acetate, a cyclic transition state involving a ternary complex between the carbonate, the alcohol and the catalyst is formed. Then, the reaction proceeds through a concerted mechanism to generate a post-reaction complex, following an addition/elimination mechanism.[74] Direct ester-carbonate interchange have also been reported[81] and described as following an associative pathway as well.

Boronic esters

Cyclic boronic esters, also known as dioxaborolanes are synthesized by condensation of boronic acids with 1,2- and 1,3-diols leading to 5- and 6-membered rings respectively.[82-84] Boronic acids are used in a wide range of reactions in organic chemistry, as catalysts, pronucleophiles (cross-coupling reactions) or reaction intermediates.[82,85] In carbohydrate chemistry, they are also useful as protective groups for diols and diamines.[82,85,86] Besides, their ability to bond with diols makes them particularly useful in biology, biochemistry or chromatography for sugars and diol-bearing compounds purification or carbohydrates sensors for example.[85,87-89] In medicine they are also proposed for drug delivery[90-92] and glucose sensing for diagnostic purposes.[93,94] The key feature of boronic esters is their

reversible formation from diols and boronic acids resulting in dynamic systems with tunable properties. In biological media, this reactivity results in a dissociative mechanism, as boronic esters in aqueous conditions are prone to hydrolysis yielding boronic acids.[95,96] The equilibrium between dissociated boronic acid-diol and associated boronic ester (Scheme 4), was exploited to prepare covalently crosslinked self-healing hydrogels for example.[97-99]



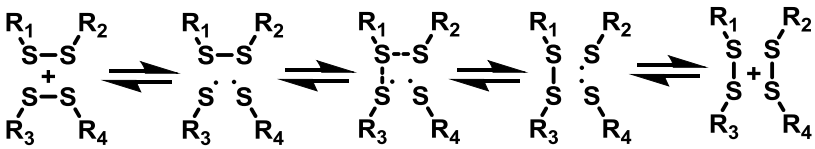
Scheme 4. Equilibrium between boronic acid and 1,2-diol and cyclic boronic ester.

Over the past few years, growing interest for this functionality has spread in the polymer science community, in particular for the preparation of self-healing polymers.[100,101] Interestingly, Sumerlin et al.[101] showed that two different mechanisms are involved in the exchange reactions occurring in boronic ester-based crosslinked materials. The exchange occurs either via classical boronic ester dissociation and re-esterification, or via an associative mechanism similar to transesterification, provided that free diols functions are available in the material. As the dissociative mechanism requires water to cleave the boronic ester, it is assumed that in a completely dry environment, only the associative transesterification mechanism occurs.[85,102] Guan et al. implemented this associative mechanism in the first boronic esters crosslinked vitrimers.[44] Eventually, Nicolaÿ, Leibler et al.[103] reported a vitrimer based on a third kind of exchange reaction, namely the direct metathesis between two boronic ester moieties. Although the exact mechanism of this reaction remains uncertain, the hypothesized transition states and intermediates are expected to have a higher connectivity,[104] as expected for an associative mechanism. Raynaud et al. investigated the mechanism at work in dynamic polymer networks based on pinacol boronates. The experimental and theoretical results corroborate the hypothesis of an associative mechanism as suggested, and that the reaction is triggered by adventitious traces of nucleophiles trapped in the medium.[105] Nevertheless, mechanistic studies would be very useful to confirm the associative pathways of boronic esters exchange reactions in anhydrous conditions and to acquire the knowledge required to harness this type of exchange reaction more efficiently.

Sulfur-containing bonds

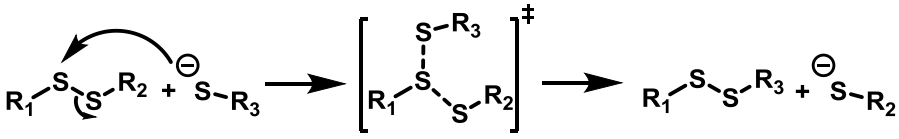
Disulfides

For a long time, disulfide bonds have been known to feature an interesting reversible behaviour. Historically, this behaviour has been used in personal care products. Disulfide bonds naturally occurring in keratin were cleaved by a reducing agent before new bonds were generated using an oxidant to perform so-called “permanent wave” on hair.[106] This process can be considered as an early chemically-reshapable material and was implemented after several decades in reversibly crosslinked polymers.[107,108] Disulfide bonds are also involved in the rubber vulcanization process. Hence, in 1946, Stern and Tobolsky already discussed possible mechanisms for the reshuffling of these bonds to explain stress relaxation in these materials.[109] The mechanism remained uncertain but usually admitted to be associative.[104] Two possible mechanisms have been discussed: 1) a [2+2] metathesis mechanism, and 2) a radical-mediated [2+1] mechanism, where a S-S bond would be homolytically cleaved prior to a radical attack of another S-S bond to yield a 3-membered intermediate (Scheme 5).



Scheme 5. Disulfide exchange [2+1] radical mechanism.

To elucidate which mechanism was involved, *in silico* studies were carried out, and concluded that the radical mechanism was more likely to occur.[110-112] This conclusion was verified experimentally by model exchange reactions in the presence of radical traps or radical sources.[113] However, when a nucleophilic catalyst is used, two mechanisms occur simultaneously, the radical mechanism described previously, and a thiol-mediated exchange due to the formation of thiolate anions. Moreover, UV light can advantageously activate disulfide metathesis. Thus, materials exhibiting self-healing behaviour upon 5-min exposure to 320-390 nm UV light were synthesized.[114] Although this reaction is convenient to yield self-healing materials,[114-116] its dissociative mechanism may not be suitable to obtain vitrimer properties. Additionally, disulfide metathesis is not always the only mechanism involved. Hence, depending on the synthetic pathways for disulfide-containing polymers and on the stoichiometry chosen, dangling thiol moieties enable thiol/disulfide exchanges. For this reaction the exchange proceeds through an associative mechanism, whereby a disulfide bond is attacked by a thiolate, yielding a new disulfide bond through a 3-membered transition state (Scheme 6).[111,117] Thus, attention should be paid to stoichiometry when designing a disulfide-containing vitrimer or self-healing material.



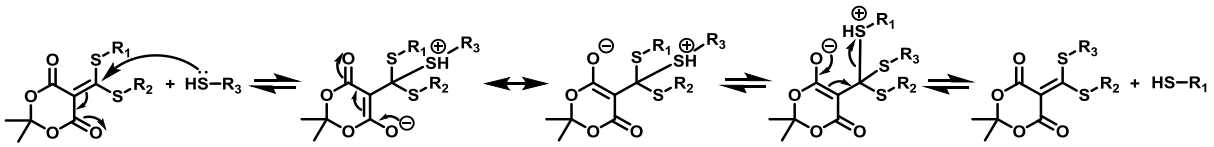
Scheme 6. Thiol-disulfide exchange mechanism.

Thioesters

Recently Bowman et al. reported thioesters dynamic networks.[118] Without neighbouring groups the exchange takes place via a purely associative pathway. Nevertheless, when NGP were present, two competitive mechanisms were discussed: a mechanism involving an equilibrium between the associated thioester form and the dissociated thiol / anhydride form; and the associative transthioesterification mechanism requiring free thiol moieties.

Meldrum's acids

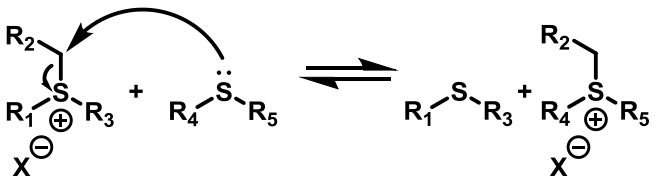
Sulfur-bearing Meldrum's acids were also described as exchangeable crosslinkers in PDMS vitrimers through an associative mechanism involving thiol moieties (Scheme 7).[119]



Scheme 7. Mechanism of Meldrum's acid exchange with a thiol on an example.

Trialkylsulfonium salts

In the 1970s, a group at Ghent got interested in poly(propylenesulfide) and the mechanism of its degradation upon incorporation of oxonium salts to introduce sulfonium groups in the material. They reported an exchange reaction between thioethers and trialkylsulfonium likely proceeding through an associative mechanism whereby the sulfur atom of the thioether attacks the α-carbon atom of a sulfonium salt prior to the elimination of the exchanged thioether following an associative pathway (Scheme 8).[120-123] The fact that sulfides react with electrophiles (brosylates for instance) and the positively charged sulfonium is a good leaving group comfort the hypothesis of a S_N2 mechanism, while a S_N1 is unlikely considering this pathway would involve a highly unstable primary carbocation. Four decades later, the group of Du Prez studied and updated this forgotten chemistry and implemented it in polythioether networks to prepare catalyst-free vitrimers.[40] Knowledge on this bond exchange chemistry remains scarce, but the promising opportunities offered in rubber recycling[124] might favor more in-depth studies.



Scheme 8. Proposed mechanism for thioether-sulfonium exchange.

Silyl ether transalkoxylation and metathesis

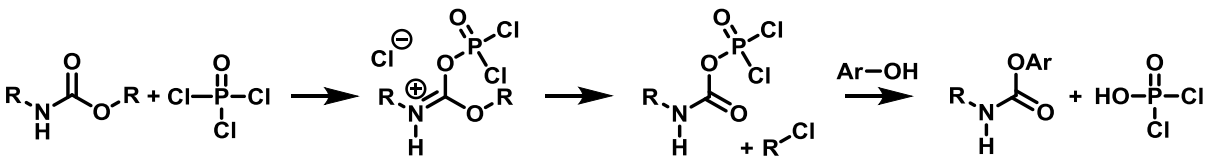
Silicones represent an $11-billion industry and production of formulated silicones exceeded 2Mt in 2013.[125] Silicones are made from silicon, which is also the main component of glass. In the 1950s, polydimethylsiloxanes (PDMS) were reported to exhibit stress relaxation behaviour thanks to a chemical phenomenon of chain exchange, catalyzed either by an acid or a base.[126,127] The acid-catalyzed mechanism was supposed to involve a protonated oxygen atom on the Si-O-Si bond as an intermediate,[127] but this mechanism still seems unclear. The base-catalyzed mechanism was supposed to involve the attack of the basic species onto a silicon atom consequently cleaving a Si-O-Si bond and yielding an anionic $^{-}$O-Si group.[127] However, the mechanism leading to the exchange between two polymer chains was not fully elucidated. Surprisingly, the self-healing properties of these materials were somehow forgotten, except for a patent reporting thermally reversible silicone rubbers catalyzed by strong acids, becoming malleable at 150 °C but remaining insoluble and dimensionally stable at room temperature.[128] The self-healing behavior of polysiloxanes was rediscovered in 2012 by McCarthy et al.[129] after the concept of vitrimer was first defined. They studied tetramethylammonium dimethylsilanolate–terminated polysiloxane chains and emphasized that any crosslinked PDMS elastomer could be converted into a self-healable polymer by addition of basic catalysts. The mechanism involved is an associative trans-siloxanation. The first step of this mechanism would be the dissociation of the chain-end silanolate-counterion ion pair followed by the attack of the silanolate anion onto a silicon atom and simultaneous cleavage of a Si-O bond (Scheme 9).[130,131] Thus the ion pair would behave as a dormant species, and the silanolate anion as the active one enabling chain exchange. Other strong bases can be used to generate living chain ends such as the most effective potassium hydroxide and cesium hydroxide, but a major flaw at high temperature is the formation of volatile cyclic oligomers leading to decreases of connectivity and average molar mass.[131] In 2017 Guan et al. used a silyl ether as the exchangeable moiety in crosslinkers to make polystyrene networks, where the exchange reaction involved free hydroxyl groups without ion pairs.[45] Finally, the same group reported an exchange reaction in the absence of free hydroxyl

moieties and hypothesized a direct silyl ether metathesis mechanism catalyzed by acids, but the mechanism still remains unclear and further investigations are needed to fully understand the behaviour of this material.[132]

Scheme 9. Trans-siloxanation mechanism.[130]

Urethanes, ureas, thiourethanes and hydroxyurethanes

Polyurethanes (PU) are the 5th largest production of industrial polymers with a global production reaching 20Mt/y.[133] The urethane bond, alternatively called carbamate, is usually obtained by reaction between an isocyanate and an alcohol, and has been known to be reversible at high temperatures for a long time. Ureas are obtained by reaction between isocyanate and amine, and the direct condensation of ureas leads to biuret functions. In the 1950s PU materials were shown to exhibit stress relaxation thanks to urethane cleavage.[134] Furthermore, relaxation times were shorter when the material included ureas and biuret bonds,[135] highlighting the increased reactivity of nitrogen in exchange reactions. Catalyst-free vitrimers based on exchangeable urea bonds were also made thanks to bulky groups, which enhances their reactivity toward urea-urea exchange without the need of any catalyst.[136] Nevertheless, the mechanism involved in this process is uncertain. In the early studies on urethane cleavage, the mechanism was suggested to be dissociative, involving the dissociation of the urethane to its initial isocyanate and alcohol moieties,[137] as no free hydroxyl groups was available for transurethanization reaction.[138,139] Even when a free alcohol is available next to a urethane bond, the dissociative pathway occurs most of the time, in some cases along with an associative pathway similar to transesterification (Scheme 1), depending on the system composition and temperature. A low temperature favors the associative mechanism and reversely, high temperatures favor the dissociative one.[137] In solution, external catalysts such as phosphoryl chloride were shown to favor the associative mechanism between a urethane and a phenol over the dissociative one (Scheme 10).[140] The direct exchange between two urethane moieties *via* an associative mechanism has been ruled out.[139]

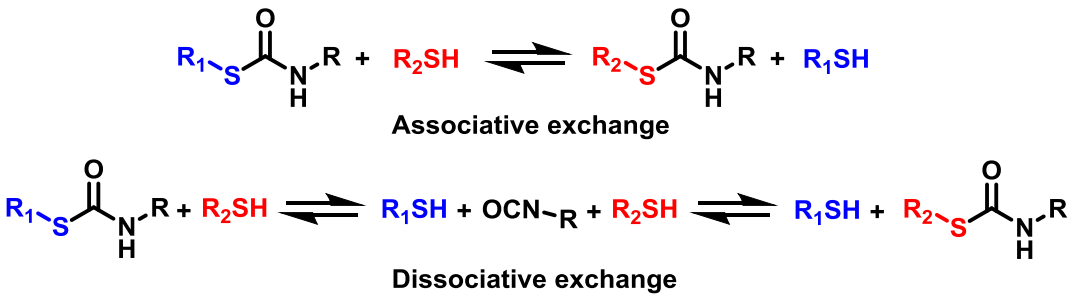


Scheme 10. Phosphoryl chloride as a catalyst favors the associative mechanism of transcarbamoylation with phenols.[140]

Ureas seem to be promising bonds to implement in self-healing materials as the exchange reaction is much faster.[135] However the exchange mechanism is similar, with first, a dissociation (which rate depends on the steric hindrance of the amine) yielding the starting isocyanate and amine.[141-143] Thus, based on their apparent dissociative mechanism, polyurethanes and polyureas do not seem to be suitable to obtain vitrimer properties.

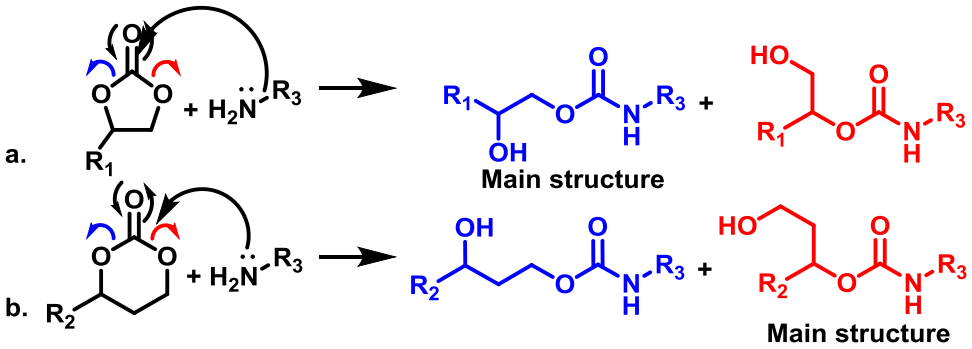
Recently, polythiourethanes (PTU) started to be investigated to make self-healing materials. PTU vitrimers catalyzed by dibutyltindilaurate were synthesized by reaction of a trithiol with different diisocyanates: isophorone diisocyanate, 1,6-diisocyanatohexane or tolylene-2,6-diisocyanate. In these materials, the structure of the isocyanate precursor influenced the relaxation time. Aliphatic

isocyanate-derived networks displayed much higher relaxation times at 180°C than their aromatic analogs. The relaxation times of isophorone diisocyanate- or 1,6-diisocyanatohexane- derived network were 11.1 mins and 10.7 mins respectively whereas it was only 2.9 mins for the aromatic tolylene-2,6-diisocyanate-based material. Both associative and dissociative exchange mechanisms were reported to be involved in their reprocessability (Scheme 11).[144,145]



Scheme 11. Associative and dissociative exchange pathways for polythiourethanes.[144,145]

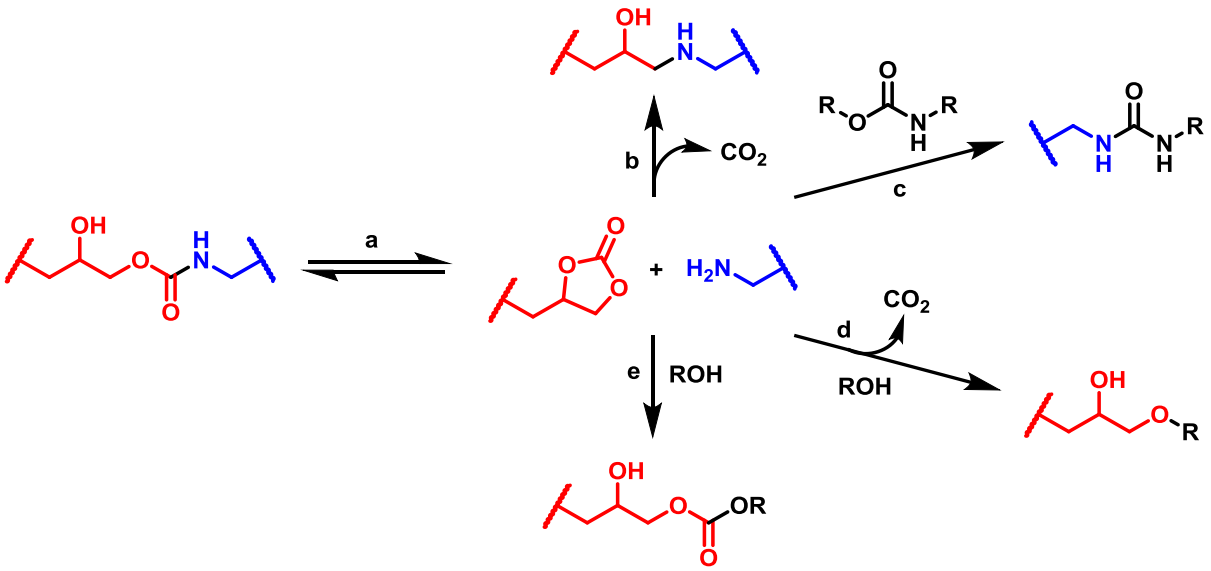
Compared to traditional PU, the case of polyhydroxyurethanes (PHU) prepared from cyclic carbonates and amines may be different. PHU contain hydroxyurethane bonds, that are carbamate bonds with a hydroxyl group at the β- (Scheme 12) or γ- positions. The synthesis of these materials is advantageously greener compared to PU, as it does not involve the use of isocyanates which are toxic substances.



Scheme 12. Synthesis of polyhydroxyurethanes (PHU) from: a. 5- and b. 6-membered cyclocarbonates featuring a substituent on the β-position.

Fortman et al. studied PHU vitrimers and suggested that transcarbamoylation occurred, albeit slowly, and that decomposition and side reactions occurred more easily at high temperatures.[146] In particular, side reactions were observed at 160 °C and over, whereas the decomposition of the urethane linkage to an isocyanate and an alcohol usually occurs over 250 °C. These observations were highly dependent on the type of PHU: 5-membered cyclocarbonates-derived PHU (5-CC PHU, Scheme 12a) were more prone to decomposition *via* dissociative reactions at 180 °C. 5-CC PHU were shown to decompose back to their 5CC amine precursors (Scheme 13a). Several decomposition reactions were hypothesized: reaction of amine with cyclic carbonates by irreversible decarboxylative mechanism (Scheme 13b), addition of amines to carbamates to form ureas (Scheme 13c), decarboxylative reaction of free hydroxyl groups with cyclic carbonate to form ethers (Scheme 13d) or carbonates (Scheme 13e), and oxazolidone formation, to name a few. These irreversible reactions are responsible for the loss of mechanical properties of the reprocessed materials. On the contrary, the dissociative reversion reaction leading to the starting amine and cyclocarbonate was not observed for 6-CC PHU (Scheme 12b), thus limiting the decomposition reactions. This suggests

that the associative transcarbamoylation may be responsible for the stress-relaxation behaviour observed for these 6-CC PHU materials.[139,147]



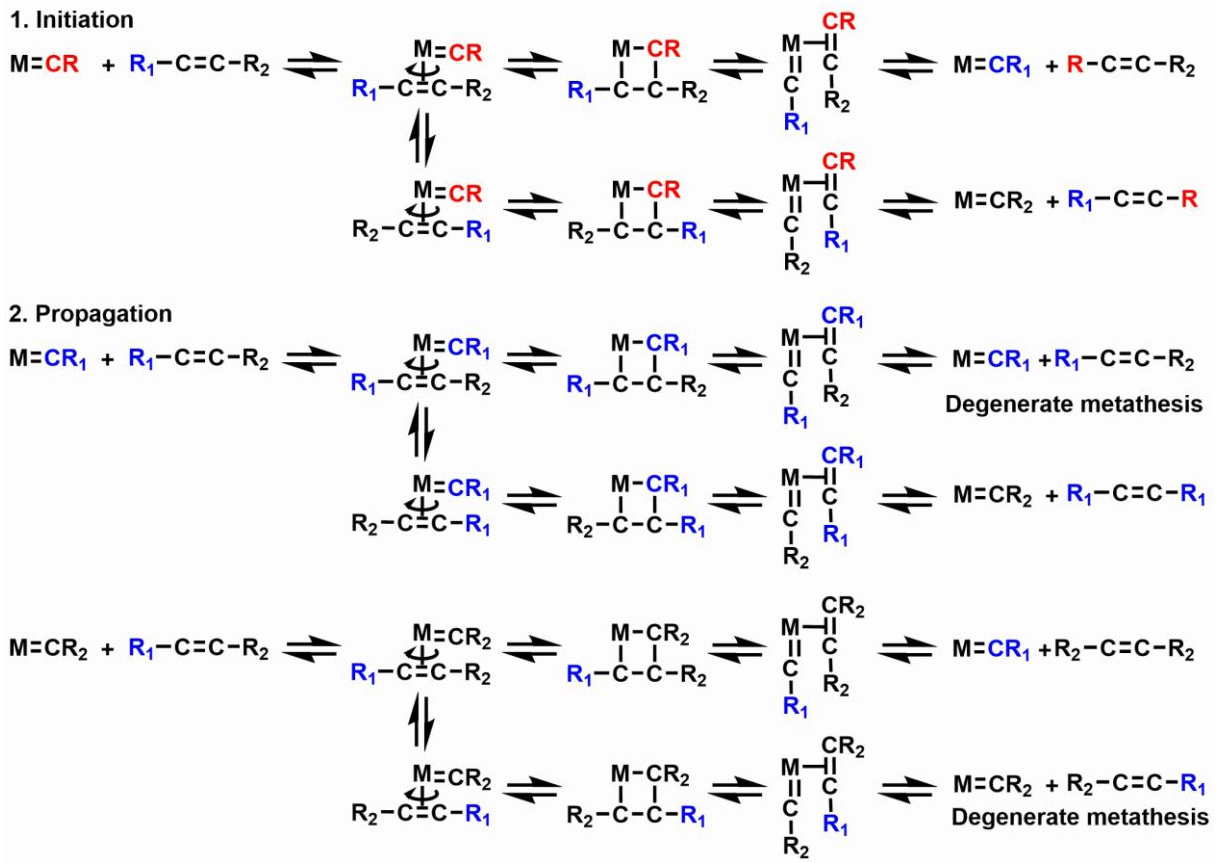
Scheme *13*. a. reversion of 5-CC PHU to the original 5-CC and amine and hypothesized decomposition reactions b. by decarboxylation, c. by formation of urea, d. by formation of ether and e. by formation of carbonate.[147]

Chen et al. also pointed out that two simultaneous mechanisms were responsible for the network rearrangement of their 5-CC PHU, the associative transcarbamoylation and the dissociative reversible cyclocarbonate aminolysis, yielding back the initial cyclocarbonate and amine.[148] Because two main reactions seem to be accountable for the stress relaxation behaviour of PHU and PTU, and because one is associative whereas the other is dissociative, one can rule out this chemistry for associative CANs. However, more research could be done to favour the associative mechanism over the dissociative one, investigating the effects of catalysts, the network morphology or the monomer structure, for example.

Olefin metathesis

In the early days of petrochemistry, investigations led on propane cracking revealed that cracking of propylene at 752 °C under 0.2 atm yielded 23-24 mol% of butylene and ethylene.[149] The overall reaction equation is similar to a metathesis. However, this reaction is inexploitable under such conditions that do not allow any control. Olefin metathesis was then developed in the 1960s by chemists working for DuPont and has been extensively studied for both industrial production and research purposes.[150-152] Olefin metathesis requires metal catalysts to occur quantitatively. An in-depth discussion on these catalysts is out of the scope of this article, but a rich literature as well as very relevant books are available.[150,152] At first glance, the overall reaction seems to be rather simple and can be summarized as a carbene exchange between two olefins. Nevertheless, the underlying mechanism involved is complex. Yves Chauvin, Richard Schrock and Robert Grubbs were awarded the Nobel Prize in Chemistry in 2005 for elucidating this mechanism, developing the first catalysts and synthesizing more convenient catalyst, respectively.[153-155] Their studies deepened the knowledge of this exchange reaction, which was useful to develop new catalysts. Indeed this reaction fully relies on metal-carbene catalysts. The mechanism of olefin metathesis is detailed in Scheme 14.[150,156-159] All

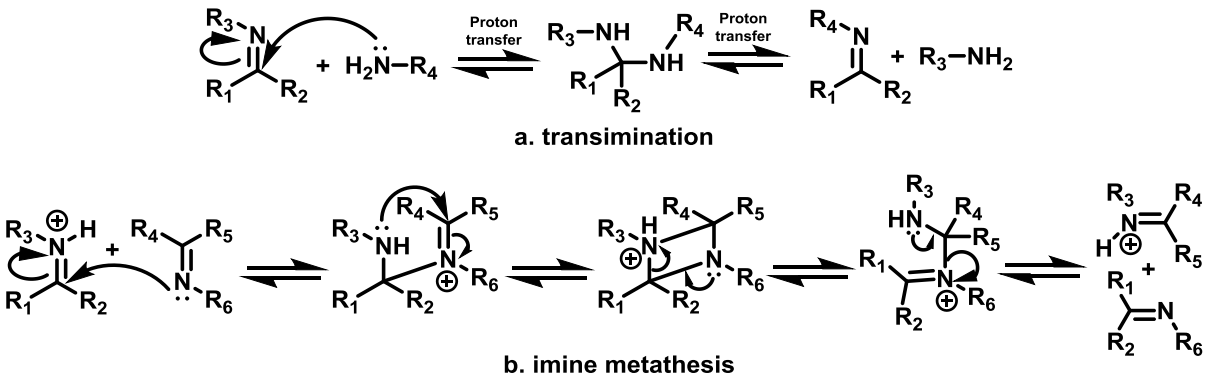
the steps for this reaction are equilibria, so if the reactants and desired exchanged products have a similar enthalpy, the reaction is degenerate. This property is convenient to make exchangeable crosslinks in vitrimers. In contrast, when metathesis is used for organic synthesis, aiming at efficient synthesis of a desired exchanged olefin product, the equilibrium can be easily displaced by using a R-CH=CH_2 olefin as the substrate. Thereby, the direct reaction yields the desired product and easy removal of ethylene from the reaction vessel provides the necessary driving force for the reaction to happen preferentially in the desired direction. An example of polybutadiene vitrimers implementing olefin metathesis as the exchange reaction was reported.[160,161] These materials were made of crosslinked polybutadiene by reaction of butadiene with benzoyl peroxide. The interest of polybutadiene is the presence of insaturations in the network after crosslinking. These insaturations can undergo olefin metathesis in the presence of a Grubbs catalyst. Therefore, it is possible to make a vitrimer by adding a Grubbs second-generation catalyst before the polymerization, but a much more original approach is to make a vitrimer out of a thermoset by swelling it with a solution of the catalyst after the crosslinking process. Such strategy to make vitrimers has so far been specific to olefin metathesis vitrimers. These vitrimers exhibited self-healing at ambient temperature and below. Self-healing behavior was also observed for thermoset materials after the catalyst was only applied on the surface where healing was required. When no catalyst was used, no effective self-healing was observed. In summary, olefin metathesis allows original strategies to make vitrimers, which is not possible with other chemistries. However, the use of a metal catalyst seems unavoidable and could be seen as the major drawback of this exchange reaction.



Scheme 14. Olefin metathesis mechanism.[150]

Imines

Imines result from the condensation of an aldehyde or a ketone and a primary amine to obtain a C=N bond. Imines were investigated in the field of biochemistry, as their reversible covalent bond is known to be involved in enzymatic reactions,[162] and more recently in the field of materials chemistry,[163-175] with the growing interest in dynamic covalent networks. Actually three exchange reactions are known for imines : a dissociative hydrolysis followed by reaction with another amine; an associative exchange between an imine bond and a free amino moiety called transimination; and a direct associative imine-imine exchange referred to as imine metathesis.[166,170] Obviously, only the latter two associative reactions are interesting for associative CANs design. Although dissociative hydrolysis may happen in imine-based vitrimers, if the amount of water in the polymer matrix remains low, this reaction is unlikely to influence significantly the properties of the material. Therefore, the focus here is put on transimination, which requires residual amines, and on imine metathesis, which does not. Transimination has been known to occur through an equilibrated associative pathway for several decades.[176,177] Three successive steps were described. The first and rate-determining step consists in the attack of a free primary amine on the imine carbon atom to form a geminal diamine tetrahedral intermediate.[162,178-181] Then, two protons transfer from the nitrogen atom of the formerly attacking amino moiety to the nitrogen atom of the formerly imine moiety.[162,179,181] Finally the exchanged amino moiety dissociates and leads to the formation of the new imine.[162] (Scheme 15a) The mechanism of imine metathesis is less extensively studied, but is described as a nucleophilic addition of a neutral imine to a protonated one. The reaction proceeds through a 1,3-diazetidinium intermediate yielding the exchanged imines or the initial reactants.[179,182] (Scheme 15b) Transimination and imine metathesis have already been implemented in various polymeric materials to make vitrimers directly from polyimines[163,165,167,169] or using imine bonds to crosslink polyesters,[166,172,173,175] polybutadiene,[164,168] polydimethylsiloxanes[171] and polyethers.[174]

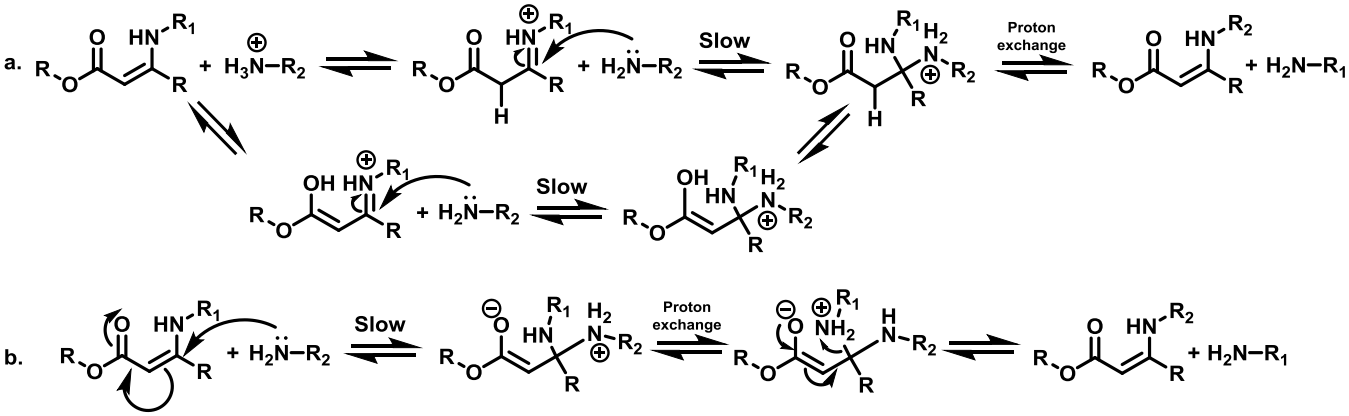


Scheme 15. a. transimination and b. imine metathesis mechanisms.

Vinylogous urethanes, ureas and amides

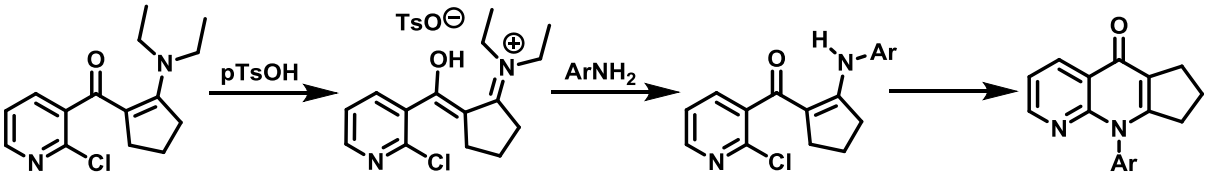
In the late 1970s, the exchange of amine moieties on enaminone structures was reported.[183] Later in the 1990s, similar exchanges between dialkylamine-derived enaminones and aromatic primary amines were discussed.[184,185] However, this exchangeable bond was not been implemented in polymers until 2014.[186] Moreover the mechanism involved in this first example was based on a reversible hydrolysis to the amine and carbonyl components, although a possible "component exchange" (amine direct exchange) was evoked by the authors. In this field of chemistry, enaminones are commonly referred to as vinylogous urethanes, vinylogous ureas and vinylogous amides depending on their structure. These structures are easily prepared by acetoacetylation of polyols

followed by reaction with a primary amine.[18] In 2015 Denissen et al.[18] reported the first vinylogous urethane vitrimer, exhibiting relaxation times as short as 85 s at 170 °C without the need of any catalyst. The exchange mechanism was later described by the same team[187] and depends on whether the medium is acidic, neutral or basic. In neutral and acidic conditions, the free primary amine is protonated to form an ammonium, and the ammonium-enamine couple is in equilibrium with the amine-iminium couple. The latter couple can evolve by reaction of the nitrogen atom of the amine with the iminium to form a geminal amine-ammonium tetrahedral adduct similar to the intermediate described earlier for transimination. Then, dissociation occurs, yielding either the exchanged products or the reactants (Scheme 16a). The amine-iminium pathway written in Scheme 16a (bottom) for a Brønstedt acid can be extended to Lewis acids. Under these conditions, the reaction can proceed through a zwitterionic intermediate.



Scheme 16. Vinylogous urethane transamination mechanism a. in acidic and neutral conditions and b. in basic conditions.

For instance, Friary et al.[184] studied the transamination of an enaminone bearing alkyl substituents with an aromatic primary amine in solution. The exchanged enaminone was then able to cyclize. When one equivalent of toluenesulfonic acid was added, the overall yield increased from 29 to 56 %. The authors suggested that the acid accelerated the enaminone transamination step (Scheme 17). The catalyst protonates the oxygen atom of the enaminone and generates an iminium tosylate, more electrophilic towards the attack of the amine.

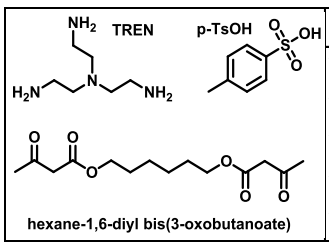


Scheme 17. Diketoenamine transamination catalyzed by p-toluenesulfonic acid (p-TsOH).

The exchange kinetics can be tuned using simple additives. Brønsted and Lewis acids such as sulfuric acid, dibultyltin dilaurate (DBTL) or zinc (II) accelerate the reaction. The use of 1 mol% paratoluenesulfonic acid was reported to reduce the time to reach equilibrium from more than 1 h to less than 10 mins at 100 °C. On the contrary, non-nucleophilic bases such as triazabicyclodecene (TBD) were reported to increase the equilibration time.[187,188] In a basic environment the exchange

reaction happens but is slower and involves a direct Michael-like addition of a neutral amine on a neutral vinylogous urethane (Scheme 16b).[187,189] These mechanisms are all associative and thus suitable to obtain vitrimer properties. Some vitrimers exhibit a dual temperature response.[189,190] Interestingly their dual behavior was explained by possibly concomitant mechanisms **a** and **b** (Scheme 16), which are usually independent as they require different pH conditions. The iminium pathway would be dominant at low temperatures whereas the neutral Michael-type pathway would prevail at high temperatures.

Catalysts also have an impact on the behaviour of vitrimers. The relaxation time of vinylogous urethane materials was reported to decrease from 10 mins at 120 °C in the absence of catalysts to 2 min with 0.5 mol% of p-TsOH.[187] A recent study by Haida and Abetz[191] studied the impact of p-TsOH in vinylogous urethane vitrimers with different stoichiometries. The networks were synthesized from hexane-1,6-diylbis(3-oxobutanoate) and tris(2-aminoethyl)amine (TREN). When an excess of amine was used, the relaxation time decreased from 29 s without p-TsOH to 0.3 s with 0.05 wt% p-TsOH. Similarly, with an excess of the acetoacetate the relaxation time decreased from more than 46800 s to only 134 s (Figure 3).[191] DBTL and sulfuric acid were shown to be less effective. In the case of sulfuric acid, the sulfate anions probably form salts with the ammonium ions. In consequence, the ammonium species are less available, thus less reactive. Similarly, carboxylate anions are also known to be proton scavengers for ammonium species in non-aqueous solutions for instance.[187] When DBTL was used, the reaction activation energy dropped from 74 $kJ.mol^{-1}$ to 45 $kJ.mol^{-1}$ suggesting a different mechanism, probably via the carbonyl moiety activation of the vinylogous urethane. On the contrary, TBD increased the activation energy up to 103 $kJ.mol^{-1}$, because of proton scavenging. Interestingly Spiesschaert et al.[192] managed to incorporate acidic or basic functionalized fillers in PDMS-vinylogous urethane matrices. When 10 wt% kaolin bearing acidic groups was incorporated, the relaxation time of the resulting material decreased from 5725 s to 4650 s at 150 °C, whereas non-functional fillers were shown to increase relaxation time. Acid, basic or neutral alumina fillers were also studied. When the relaxation time for the matrix was 4000 s, the material containing neutral alumina or basic alumina displayed relaxation times of 4650 s and 4500 s respectively. On the contrary, the material made from acid alumina showed a shorter relaxation time (3600 s), in agreement with the results observed in solution (Figure 4).[192] Other kinds of catalysis were also reported and not surprisingly an excess of free primary amines in a vinylogous urethane vitrimer accelerates transamination.[189]



Reference	R (AA/N)[a]	T_g (°C)	p-TsOH	τ (s)[b]	E_a ($kJ.mol^{-1}$)[c]
VU-E_{H+}	1.0	51		80	84.9
VU-A	0.7	13		29	75.9
VU-A_{H+}	0.7	17	✓	0.3	60.3
VU-NA	1.35	-8		> 46800	-
VU-NA_{H+}	1.35	29	✓	134	75.8

Figure 3. Impact of the stoichiometry and p-TsOH catalysis on vinylogous urethane properties. [a] ratio acetoacetate/amine [b] relaxation time at 110 °C [c] activation energy. (VU-E stands for an equal ratio of amines and acetoacetates, VU-A an excess of acetoacetates and VU-NA an excess of amines).[191]

Eventually, it is important to highlight the crucial role of the backbone and crosslinking density on the behaviour of vitrimers, as already mentioned for imine vitrimers. Spiesschaert et al.[190] recently disclosed in a detailed study that the relaxation rate of various vinylogous urethane-crosslinked polyether vitrimers decreased with increasing crosslinking density. An effect on the activation energy was also reported even if a clear trend was not identified. A dual temperature behaviour was reported for polytetrahydrofuran, polypropyleneglycol and polyethylene glycol backbones, as

reported previously in perfluoropolyether.[189,190] Nonetheless this effect was not observed on polypropanediol backbone, emphasizing the influence of both the matrix type and the molar mass of the spacers. The dual mechanism discussed earlier is probably the cause for this dual behaviour.[190]

Because they are versatile and they allow short reprocessing times, vinylogous urethanes have already been implemented in various polymers networks. Many examples were reported such as polysaccharide hydrogels,[193] polysiloxanes,[188,190,192,194,195] polybutadiene,[190,196] perfluoropolyether,[189] methyl methacrylate-(2-acetoacetoxy)ethyl methacrylate copolymer,[197] polystyrene,[198] polydimethylsiloxane (PDMS)-kaolin, PDMS-alumina and PDMS-aminated silica composites,[188,192] epoxy-amine copolymers,[199] polyethers[190] and vinylogous urethane polymers bearing photodimerizable anthracene units.[200]

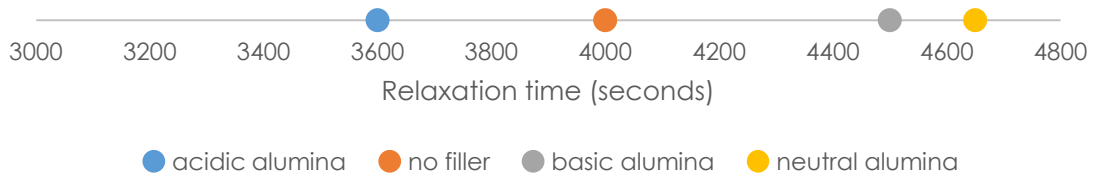
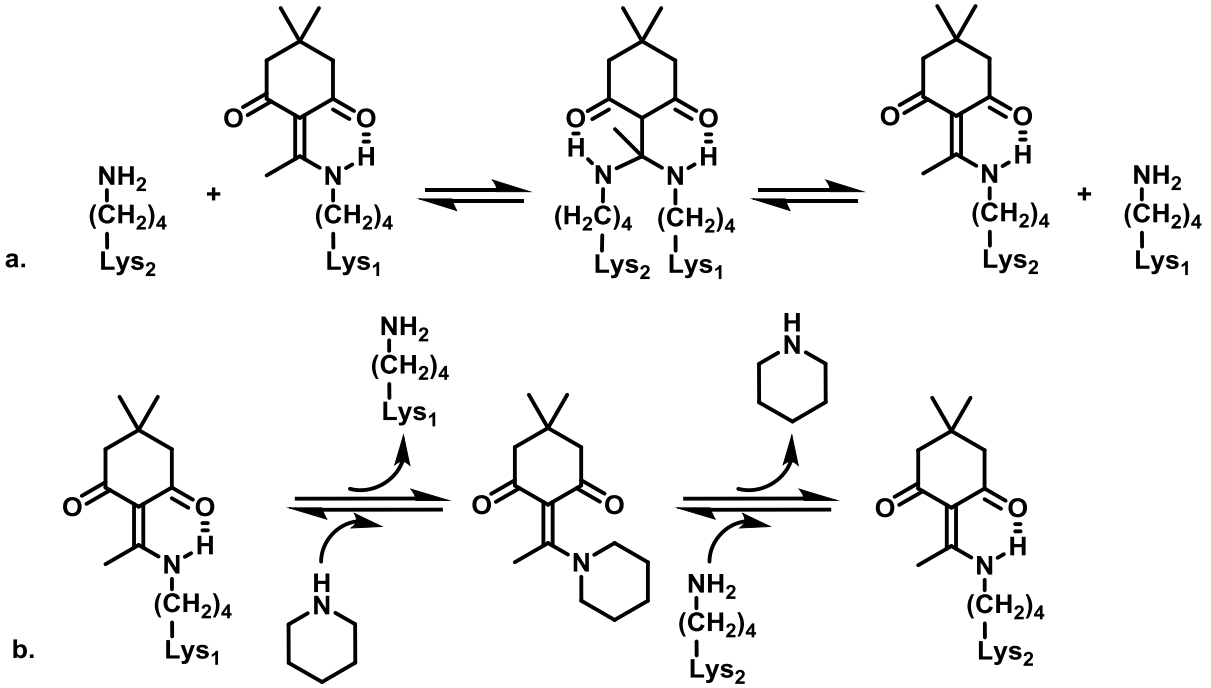


Figure 4. Effect of different functionalization of alumina fillers on vinylogous urethane vitrimer composites relaxation time.

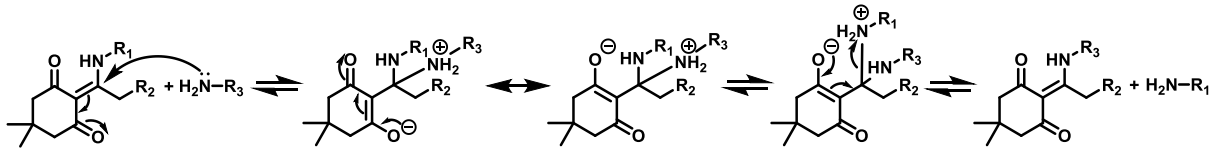
Diketoenamines

Diketoenamines are known as Dde protecting group for amines in peptide synthesis.[201,202] This protecting group is formed by reaction between 2-acetyl-5,5-dimethyl-1,3-cyclohexanedione (also known as 2-acetyldimedone) and primary amines.[203] In 2009, the behaviour of Dde was studied in detail on lysine in solid-phase synthesis. Lysine is an interesting amino acid bearing two amino moieties, in α- and ε- positions.[201] This study reported the ability of ε-NH_2 to attack a Dde-protected ε-NH_2 or α-NH_2 leading to an amine exchange. According to the authors,[201] the mechanism involves a direct nucleophilic attack of the free amine on the Dde group via a Michael addition, before a retro-Michael addition yielding either the original structure or the amine-exchanged one (Scheme 18a Scheme 19).



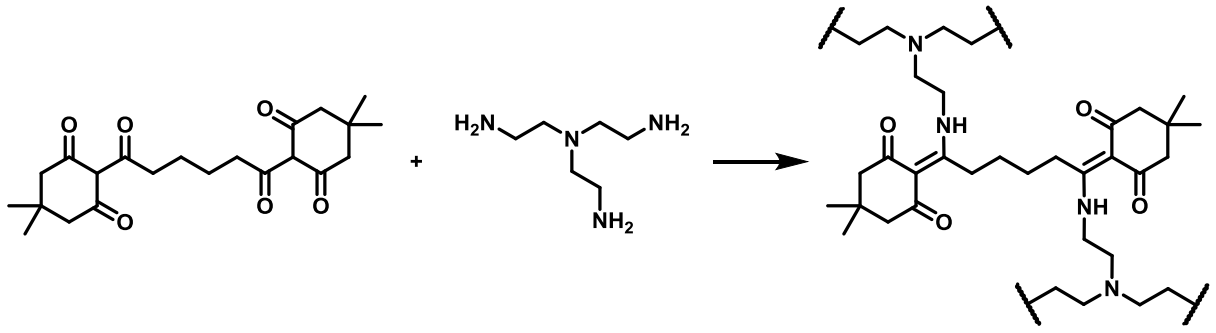
Scheme 18. Dde protection group exchange on amines a. by direct electrophilic attack b. mediated by piperidine.[201]

Another mechanism involving piperidine as catalyst was also described. Piperidine acts as a mediator to pick up the Dde group from the originally protected amine before attack of another primary amino group. The overall reaction is composed of two successive exchanges, first between the originally protected amine and piperidine and then between the protected piperidine and a free amine (Scheme 18b). In all cases, the mechanism of amine-exchange is associative.



Scheme 19. Mechanism of diketoenamines exchange.

This chemistry was implemented in materials synthesis by Christensen et al to make vitrimers.[204,205] who reported the synthesis of a network by click polycondensation between β-triketones and primary amines (Scheme 20). Triketones were synthesized from polytopic carboxylic acids and 1,3-diketones, and the final materials simply by ball-milling of the reactants at room temperature. The materials obtained were reprocessable without requiring a catalyst and followed an Arrhenius behaviour. These materials are easily hydrolysed. While this feature is often considered as a flaw, it can be beneficial for specific applications. In particular, as the materials are fully hydrolysed in a few hours at room temperature in sulfuric acid (less than 12 h in 5 M H_2SO_4), the monomers can be easily recovered. Amines are separated from the triketones thanks to an ion exchange resin, with a recovery above 90 %. The recovered monomers can be reused to make new poly(diketoenamines). This feature affords a convenient and efficient chemical recycling by hydrolysis at room temperature, while other hydrolysable vitrimers require heating and more demanding conditions.



Scheme 20. Example of synthesis of diketoenamine vitrimer. Alternatively, various diketones and mixes of primary triamines et diamines were also used.[204,205]

The range of exchange reactions suitable for the design of vitrimers is already large (Figure 2), and new exchange chemistries occurring via associative pathways are still to be implemented in such materials,[206] although proving the associative character of an exchange reaction is often challenging and remains uncertain in some cases. In addition, a survey of the activation energies of the associative exchange reactions implemented in vitrimers (Figure 5) shows that these energies can be distributed over relatively large ranges. This is certainly an asset for chemists and materials scientists who want to tune the reshaping ability of vitrimers.

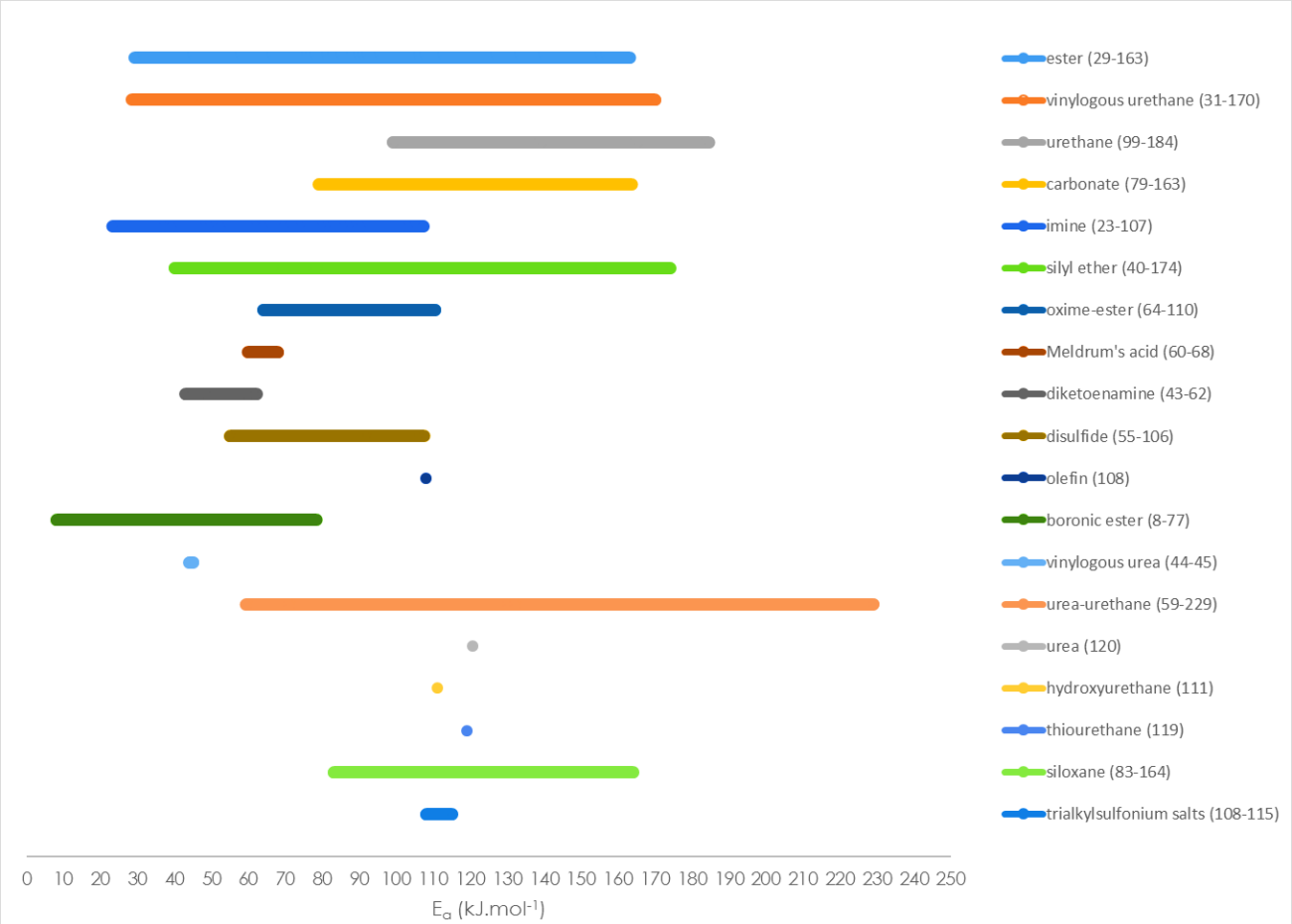


Figure 5. Activation energy ranges for exchangeable bonds implemented in vitrimers.

1

2

(III) Internal catalysis, sterics and neighboring groups effects on exchangeable bonds

Many parameters influence the properties of vitrimers: the crosslink density, the nature of the network backbone and obviously the type of exchangeable bonds for instance. For the exchange reaction to be efficient, many vitrimers rely on external catalysts. These compounds often come with some risks of leaching out of the material, or premature ageing limiting the recycling abilities of the materials. To address these problems, internal catalysis, steric effects and neighboring group participation (NGP) are valuable. For a given exchange reaction, well-designed chemical modification of the exchangeable bonds surroundings is a way to accelerate the exchange, without resorting to any external catalyst. Different effects at the molecular scale are gathered in these three concepts (Figure 6). In light of the reaction mechanisms discussed, some relevant activating groups, either already implemented in bulk vitrimer networks, or only in solution, are presented below. This should give new insights for further research in such dynamic materials.

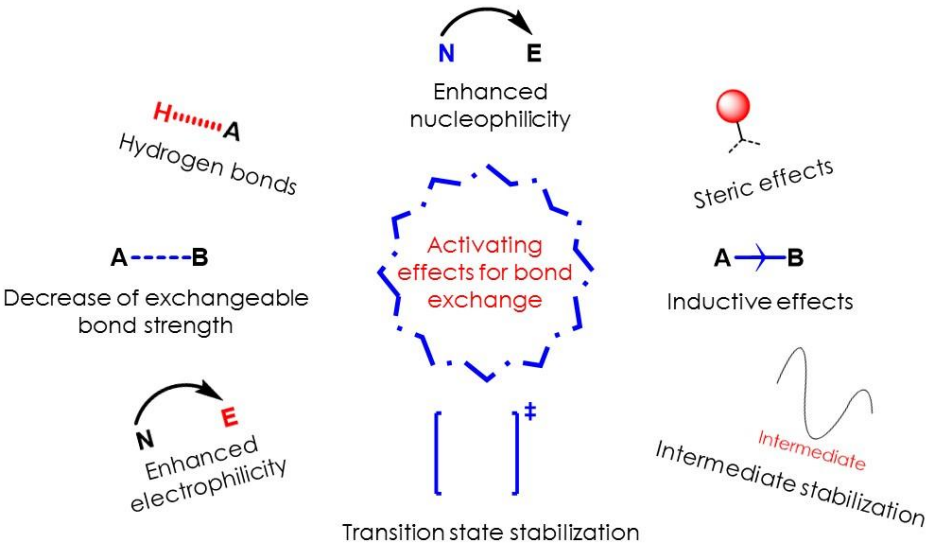


Figure 6. Examples of effects to activate bond exchanges.

Transesterification enhancement by neighboring groups: influence on the exchange mechanism and vitrimer properties

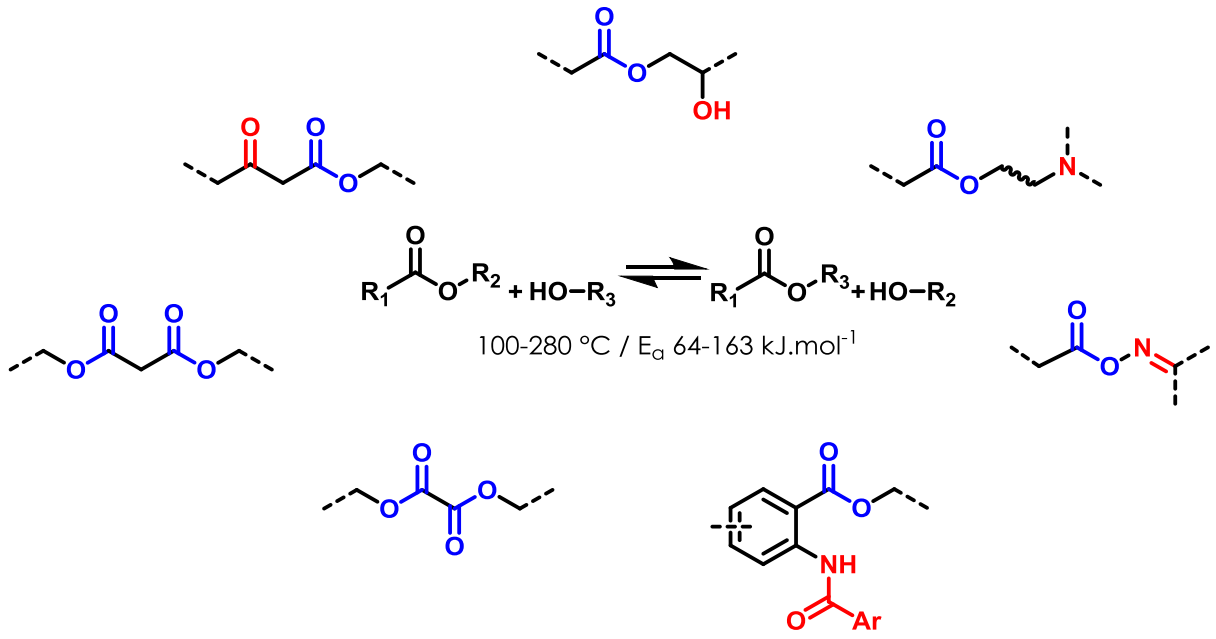
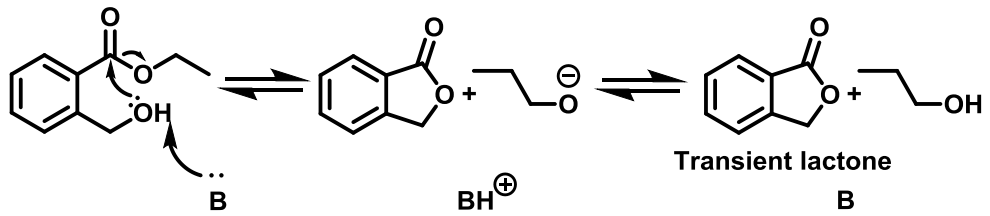


Figure 7. Main examples of activating groups activating transesterification. The temperature range[25] for stress-relaxation experiments and the range of calculated activation energies[24] of the exchange reaction in vitrimers are given.

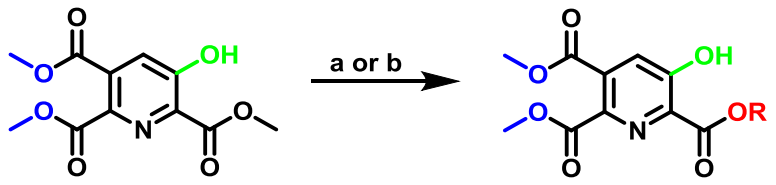
A few activating groups have been reported to influence the reactivity of esters towards transesterification and/or hydrolysis in solution (Figure 7).

For instance, on phenyl esters, a neighboring hydroxymethyl group on the ortho position increases the transesterification rate. However, the mechanism involves a cyclization after the attack on the ester by the -OH group, leading to a transient lactone (Scheme 21).[207]



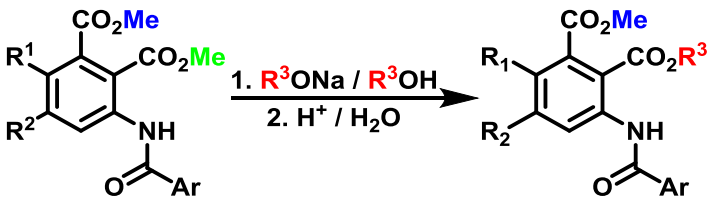
Scheme 21. Catalytic effect of o-hydroxymethyl group on phenyl esters transesterification by transient lactone formation.

This chemistry if it were implemented in a CAN would proceed through a dissociative mechanism. A regioselectivity effect is also reported on pyridine triesters as one of the ester groups possesses a hydroxyl group in ortho. Interestingly the transesterification reaction was reported to be regioselective on the ortho hydroxy ester, highlighting a reactivity increase (Scheme 22).[208] Nevertheless, in this case the regioselectivity is due to the hydrogen bonding ability of the hydroxyl group, and the mechanism is associative, contrary to the previous example.



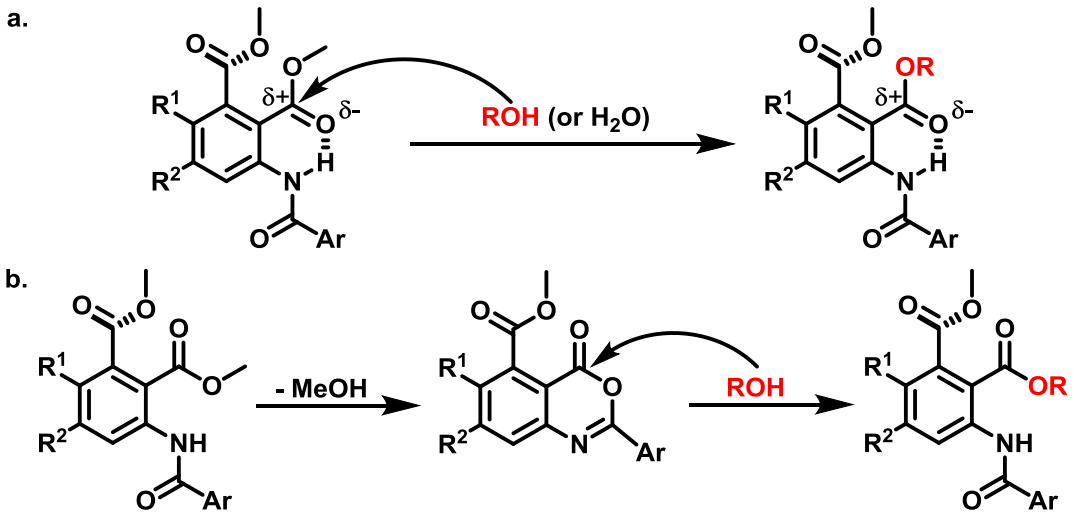
Scheme 22. Regioselective transesterification: a) 10 mol% $EtNiPr_2$, ROH, 60 °C. b) 5 mol% $Sc(OTf)_3$, ROH, cat. H_2O, 60 °C.[208]

The same kind of regioselectivity was reported with 3-benzamido-phthalates. The ester group located ortho to the amide moiety undergoes transesterification whereas that located in meta position does not (Scheme 23).[209]



Scheme 23. Regioselectivity of 3-benzamidophtalates transesterification.

Two mechanisms were discussed depending on the substituent: the first one is the regular attack of the alcohol on the ester groups activated by hydrogen bonding with the proton of the amide (Scheme 24a) and the second one is the formation of a more reactive 3,1-benzoxazin-4-one intermediate (Scheme 24b).



Scheme 24. Regioselective transesterification of 3-benzamidophtalates a. direct pathway and b. pathway with 3,1-benzoxazin-4-one intermediate.

In contrast, neighboring thioether groups stabilize the ester bond,[210] hence decreasing its reactivity toward transesterification. Fluorene structures (Figure 8) bearing a methyl carboxylate substituent on the 1-position were studied.

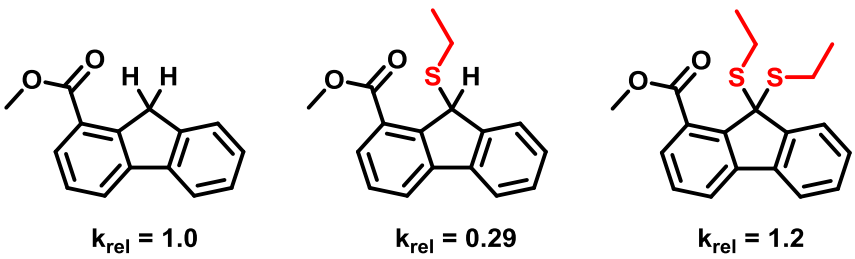
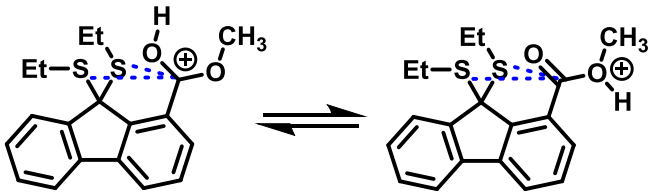


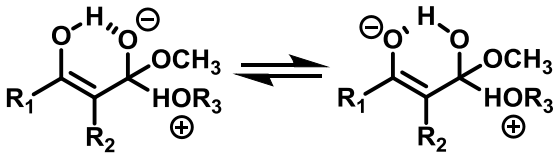
Figure 8. Effect of substitution by ethylsulfane groups on fluorene esters transesterification rate.[210]

When one ethylthio group was present on the central 5-membered ring, the rate constant of transesterification (using methanol-d_4) was 0.29 times the rate of the unsubstituted fluorene ester. Interestingly, on the fluorene ester bearing two ethylthio groups, the effect was shown to be opposite. This ester was more prone to transesterification. According to the authors of this study,[210] this phenomenon is likely due to at least two different causes resulting in opposite effects on the transesterification rate. On one hand, the steric hindrance induced by one ethylthio group would decrease the transesterification rate, as the reactive site is less accessible. On the other hand, ethylthio groups induce a stabilizing electronic effect on the protonated ester intermediate (Scheme 25). The authors hypothesized that the electronic effect were low compared to the steric effect when only one ethylthio substituent was present. On the contrary, when two ethylthio groups were present, the resulting electronic effect is significant and exceeds the steric effect, even though this effect is stronger than in the monosubstituted counterpart.



Scheme 25. Stabilizing effect of sulfur on protonated esters.[210]

β-ketoesters as well as esters derived from malonates or oxalates for example are also more prone to transesterification reactions in solution.[211] Indeed acetoacetic acid is ten times stronger than acetic acid, so its conjugated base is more stable and the corresponding ester bond is weaker leading to easier transesterification.[211] Oxalates reactivity toward transesterification is explained exclusively by inductive effects. For β-ketoesters and malonates, a stabilized cyclic intermediate was proposed to explain the reactivity of the other aforementioned species, though inductive effects also play a significant role (Scheme 26).

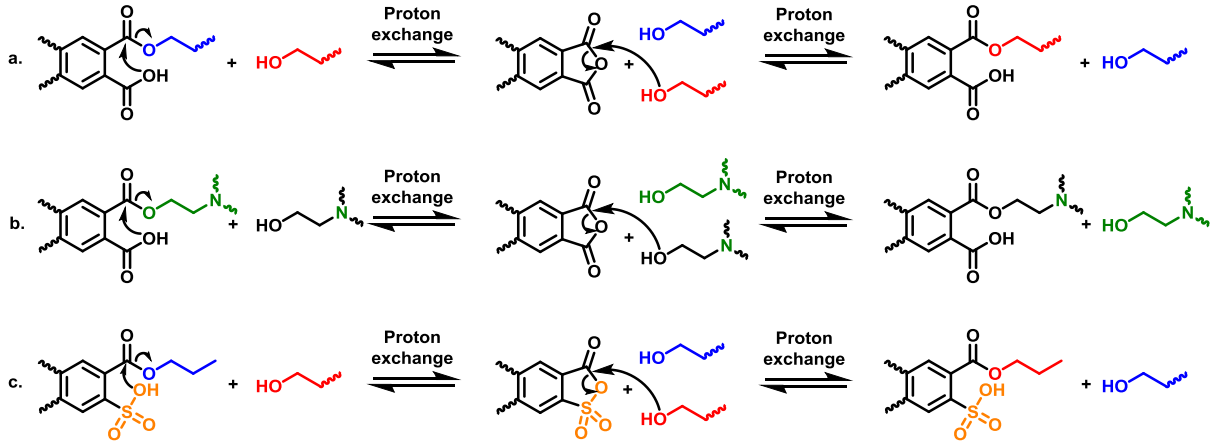


Scheme 26. Proposed stabilization by cyclic intermediate for the transesterification of β-ketoesters.[211]

Recently, diethylmalonate was used as crosslinker in a polyester vitrimer, disclosing the enhancing effect of β-activated esters.[212]

Phthalate monoesters also displayed enhanced transesterification similarly to the previously discussed o-hydroxymethyl phenyl esters,[207] as demonstrated by Du Prez et al.[47] The neighboring carboxylic acid can indeed attack the carbonyl of the ester to yield a cyclic anhydride and an alcohol (Scheme 27a). Recently the same team enhanced this effect by using a β-amino-diol with a dianhydride to make networks (Scheme 27b). The enhancing effect of β-amines had already been described for ester hydrolysis in 1962.[213] The tertiary amine at the beta position of the hydroxyl groups induced a dual activation : the neighbouring group participation of the dangling –COOH and the internal catalysis effect of the tertiary amine. The stress relaxation times decreased by a factor 500 compared to the amine-free analogous network.[214] However, it should be noted that the

mechanism was dissociative in these cases, highlighting that great care should be taken when considering neighboring groups participation as they potentially change the bond exchange mechanistic pathway.[47,214] The same mechanism was also recently reported with 2,5-bis(methoxy-carbonyl)benzenesulfonic acid, a benzoester bearing an *o*-sulfonic acid moiety (Scheme 27c).[48] These materials showed a faster stress relaxation than their carboxylic acid analogs.



Scheme 27. Dissociative transesterification pathway involving a cyclization: a. by a ortho carboxylic acid,[47] b. by a ortho carboxylic acid with an inductive effect of the beta-amino alcohol,[214] and c. by a ortho sulfonic acid.[48]

Amines were also shown to be efficient catalysts for transesterification vitrimers.[17] Triazabicyclodecene (TBD) in particular has often been used. Strategies have been designed to integrate tertiary amine groups into the polymer network. For example, bisphenol A diglycidyl ether (BADGE) was mixed with primary or secondary amines to generate epoxy-terminated tertiary amines oligomers. In a second step, the oligomers were reacted with polyacids to obtain a network bearing covalently-bonded tertiary amines (Figure 9a).[38] The exchange reaction activation energy (E_a) for this network was 93.6 kJ.mol^{-1}, very close to the 80-90 kJ.mol^{-1} range observed for the Zn-catalyzed epoxy vitrimers. Alternatively, triethanolamine was added as co-reactant in a BADGE-(methyl nadic anhydride) system for the same purpose (Figure 9b).[216] The relaxation time at 190 °C decreased from 19460 s to 4200 s when the triethanolamine content increased from 5 to 10 mol % (Figure 11).[216] Recently catalyst-free transesterification vitrimers were synthesized from a hydrogenated dimerized acid derived from vegetable oil and tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM), a tetrafunctional epoxide bearing two tertiary amino groups (Figure 9c).[217] These tertiary amines were shown to act as internal catalysts. The effect was reported to be enhanced by the flexibility induced by the vegetable oil structure. Instead of increasing monomers flexibility, dangling chains which can plasticize the material, were also shown to promote similar enhancement as tertiary amines internal catalytic effect.[218] However, a similar internal catalysis was also reported in systems based on shorter, more rigid acids and which did not contain any plasticizer.[219] These examples of internal catalysis emphasize the role of tertiary amines as promising activating groups to increase transesterification rate.

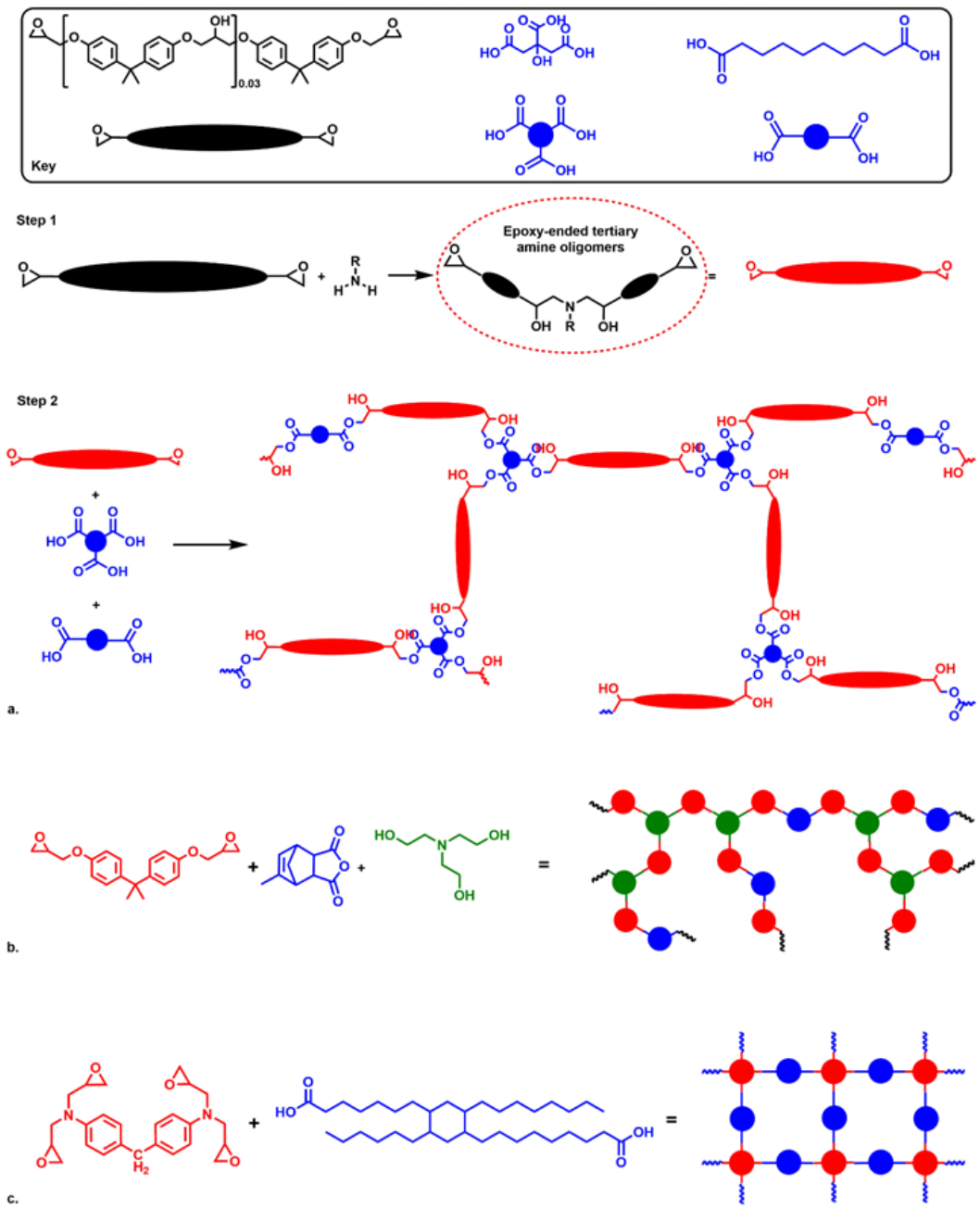


Figure 9. Strategies to embed tertiary amines in polyester networks using: a. epoxy-ended tertiary amines (2 steps),[38] b. ethanolamine as co-reactant,[216] and c. a commercial tetraepoxide bearing tertiary amines.[217]

Interestingly, a chemistry similar to the first vitrimer[1] featuring β-hydroxyesters pointed out the participation of the hydroxyl moiety in transesterification.[34,220,221] A six-membered ring with a hydrogen bond between the hydroxyl and the ester groups was hypothesized (Figure 10). The hydrogen bond is assumed to weaken the ester bond as previously discussed for the 3-benzamido group.

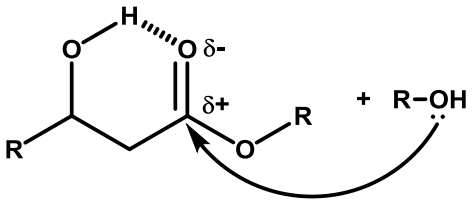


Figure 10. Hypothesized activating effect of the beta hydroxyl groups for transesterification. The hydrogen bond (dashed bond) increases the carbonyl C electrophilicity, facilitating the attack of an electrophile such as an alcohol (first step of the transesterification).

Besides, increasing the amount of free hydroxyl moieties was used to prepare catalyst-free transesterification vitrimers.[29,222] Although this effect cannot be considered as neighboring group activation or internal catalysis, it remains significant in transesterification vitrimers, was often reported in vitrimer literature, and therefore deserves to be mentioned. The acceleration of the exchange reaction can be explained by the large amount of hydroxyl groups, facilitating the transesterification by a concentration effect.[33,219] In addition, a catalytic effect is also likely caused by hydrogen bonding, as in the case of oxime-esters (vide infra). Accordingly, the addition of glycerol to an epoxy-anhydride vitrimer matrix increases the concentration of free hydroxyl groups. The concentration effect is clear as the relaxation time of the materials at 180 °C dropped from 204 mins to 86 and 66 mins for 25 mol% 50 and 75 mol% of glycerol respectively (Figure 11).[33]

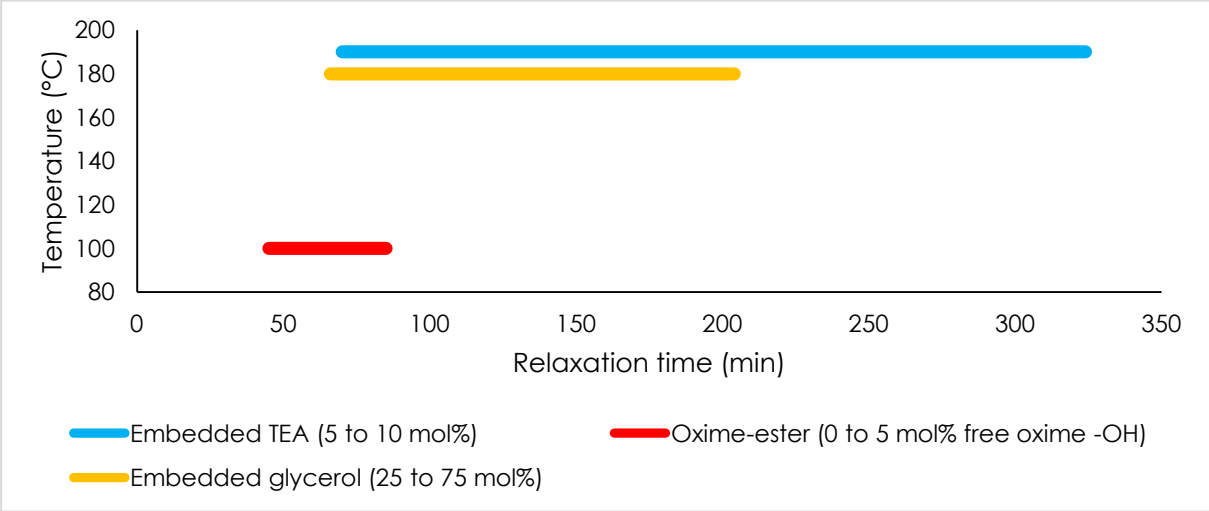
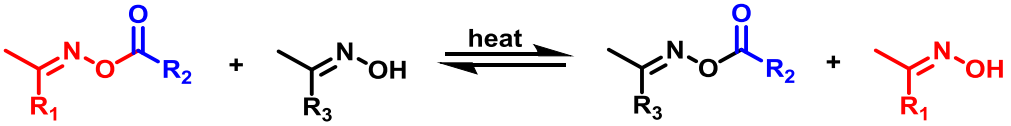


Figure 11. Effect of various enhancing strategies on stress relaxation time: hyperbranched epoxy prepolymers (HBE), network-embedded triethanolamine (TEA) and free oxime hydroxyl group in oxime-ester network.[33,216,233] Note that comparison between these 3 systems should be exerted with caution since structural parameters (backbone, crosslinking density…) differ from one system to the other..

The case of oxime-esters

Oxime-ester bonds can be considered as a subgroup of the ester family, or as a specific type of bond. The most important difference between oxime-ester and ester is the nucleophile (an oxime instead of an alcohol). Heat-induced transesterification of oxime-ester enabled the synthesis of catalyst-free vitrimers (Scheme 28),[233] with relaxation times ranging from 5102 to 2725 s at only 100 °C, depending on the free oxime-OH available and their concentrations ranging from 0 to 5 mol% (Figure

11). The acceleration of the exchange reaction is caused mainly by the high concentration of exchangeable bonds. However, part of the enhancing effect can be explained by the higher nucleophilicity of the oxime (exchangeable moiety) compared to hydroxyl groups. This would allow to decrease relaxation temperatures and times. Nevertheless, considering the scarcity of reports dedicated to oxime-ester vitrimers, it would be unwary to compare the relaxation parameters with transesterification vitrimers, as many parameters are varying between the systems reported in the literature, such as the backbone or the crosslinking density, for example.



Scheme 28. Transesterification of oxime-ester bonds.[233]

Carbonate activation by electron-withdrawing groups

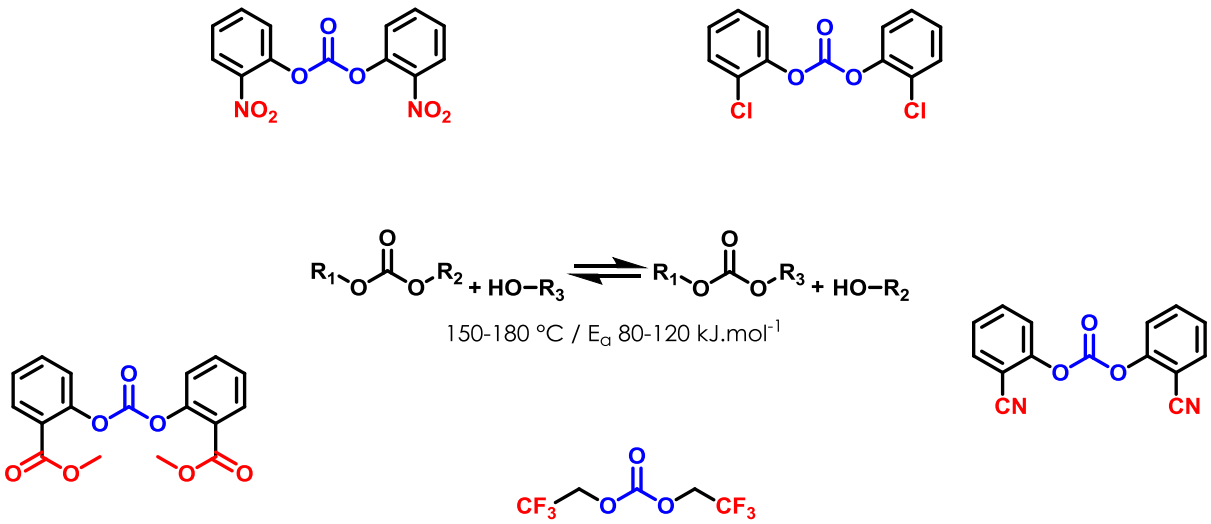


Figure 12. Examples of activating groups enhancing transcarbonation rate in solution and characteristics of reported transcarbonation vitrimers.[225-228]

Transcarbonation (Scheme 3) is used to synthesize polycarbonates, but this reaction requires a catalyst (Figure 12). Basic catalysts are probably the most used. Indeed, the generation of a more nucleophilic alkoxide increases the rate of addition onto the electrophilic carbon of the carbonate.[69,70,74,77-80] Activation of the carbonate with Lewis acids has also been reported but is less common.[74] Besides, some metal catalysts (such as tin or calcium salts for instance) that may combine Lewis acid activation of the carbonate[67,71,73,76-78] and activation of the nucleophilic alcohol[71,73,,75,77-79] have been also used. The formation of metal complexes coordinating both reacting partners increases the electrophilicity of the carbonyl[67,71,74,77-79] and also has a templating effect that accelerates the reaction. Nevertheless, neighboring groups effects on transcarbonation are still relatively unknown (Figure 12).

Inspired by a similar study on esters, Tillett and Wiggins investigated the effect of hydroxy- and methoxy-substituted phenylethylcarbonates on their hydrolysis rate (Figure 13a).[224] An influence on the hydrolysis rate could be extrapolated to transcarbonation reactions due to the strong mechanistic similarities between these reactions. At high pH, the hydrolysis rates of *o*-hydroxy-, *p*-

hydroxy- and *o*-methoxy- substituted compounds were not significantly different. However, in neutral conditions the *o*-hydroxy-substituted phenylethylcarbonate was hydrolysed ten times faster than the two other compounds. General principles for transcarbonation were given in a very complete review on carbonates in 1996.[225] Generally, the more nucleophilic alcohol displaces the less nucleophilic one and in the case of equal nucleophilicity, the less volatile alcohol displaces the more volatile one. This rule does not apply to phenols, as dialkylcarbonates react with phenols to make diarylcarbonates. In addition, alcohols bearing bulky groups or electron-withdrawing groups are poorly reactive. On the contrary, when the carbonate contains electron-withdrawing groups the alcohol exchange is accelerated. For instance fluorinated dialkylcarbonates and diarylcarbonates bearing $–NO_2$, -CN or –Cl groups on the ortho position undergo much faster alcohol exchange (Figure 13b). The activation is less noticeable when the substituents are on the para position. Brunelle et al. harnessed this effect with the use of a catalyst. Hence, they successfully polymerized orthonitrophenylcarbonates with bisphenol A at room temperature and even below[226] whereas high temperatures (up to 200-300 °C) are usually required to prepare polycarbonates.[227] The exchange between nitrophenylcarbonates and phenol was twice faster with the ortho-substituted carbonate than with the para-substituted homolog (Figure 13c). Similarly, *bis*-trifluoroethylcarbonates were shown to exchange with various alcohols and phenols in refluxing heptane or toluene (at 98 and 111 °C respectively) in the presence of a base,[225,228] and their reactivity was reported to be between the very reactive dimethylcarbonate and the less reactive diphenylcarbonate (Figure 13d).[229]

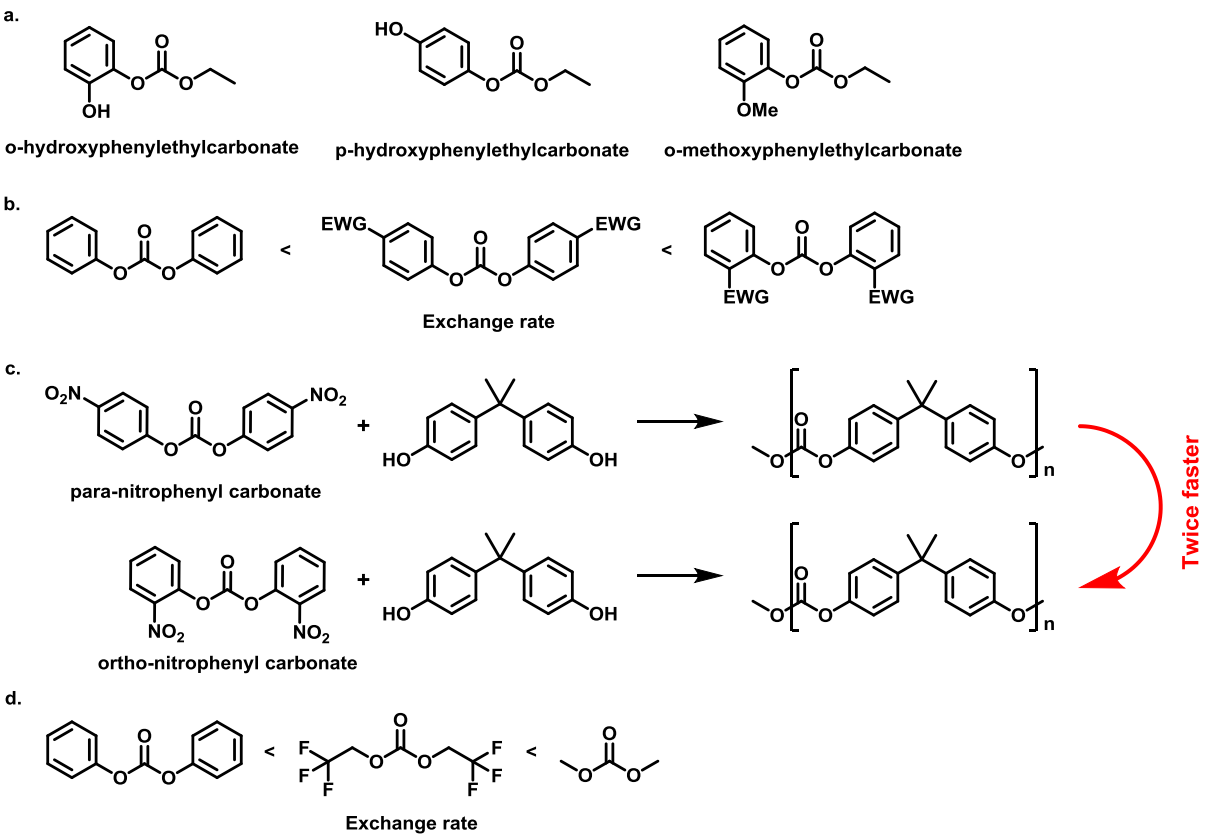


Figure 13. a. Structures investigated by Tillett and Wiggins[224] b. Effect of electron withdrawing groups (EWG) position on the exchange rate[225] c. Polymerization rate of nitrophenylcarbonates with bisphenol A depending on the substituent position[226] d. Effect of CF_3 substituent on the exchange rate.[229]

Kamps et al. studied *bis*-methylsalicyl carbonate BMSC (Figure 14) as an activated carbonate to lower the temperature for melt transcarbonation synthesis of polycarbonate.[227] BMSC was polymerized with bisphenol-A (BPA), and this polymerization was compared to that of diphenylcarbonate (DPC) and BPA. DPC-BPA polymerization was achieved in 135 minutes whereas for the BMSC-BPA system,

40 minutes were sufficient to reach similar molar masses (Figure 14). This polymerization is composed of two successive substitutions. The rates of the first and second substitutions were reported to be 30-times and 9-times higher for the BMSC-BPA system respectively. Although this study focused on the direct overall two-step reaction, the rate of the reverse reaction for the first substitution was determined for both BMSC and DPC. Indeed, the rate of the first step reverse reaction for DPC was half that of the direct reaction, whereas for BMSC it was three decades lower. The overall two-step reaction is an equilibrium. When this equilibrium was reached for the DPC-BPA system, the main product was the monosubstituted compound, and the same amounts of starting carbonate and disubstituted product were observed. In contrast, for the BMSC-BPA system, the disubstituted carbonate was the main product, the monosubstituted product was also present as byproduct whereas no starting material remained, suggesting that the equilibrium was more displaced toward the products in this case. Such observation is significant for the design of vitrimers based on exchangeable carbonate bonds.

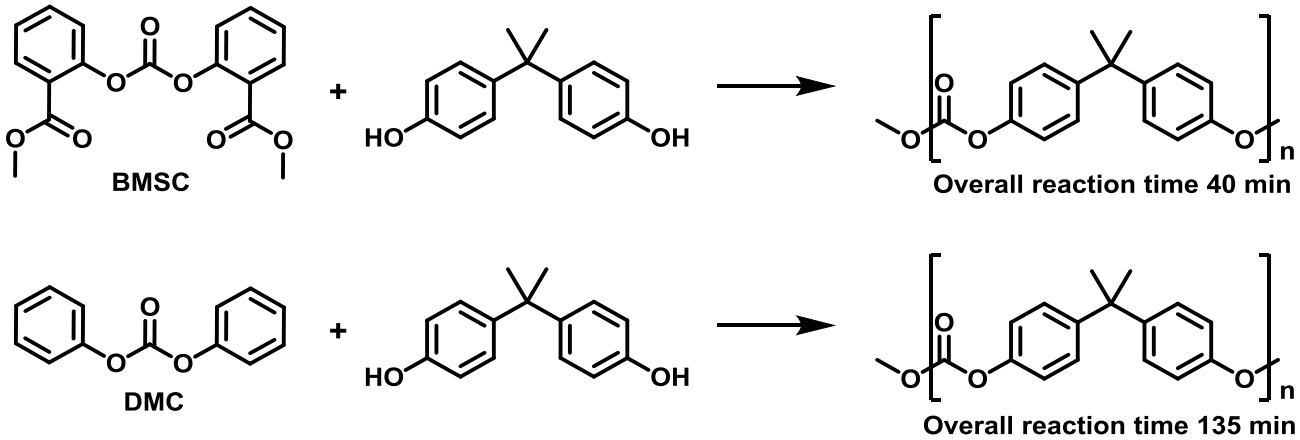


Figure 14. Polymerization of bis-*methylsalicylcarbonate (BMSC) and diphenylcarbonate (DPC) with bisphenol A (BPA).*[227]

Groups containing nitrogen seem to exert a significant activating group effect on carbonates. Amine-modified mesoporous silica prepared from amine-terminated silanes showed a catalytic effect on the transcarbonation between ethylene carbonate and methanol to produce dimethyl carbonate.[80] Thus an amino neighboring group might have interesting effects on the transcarbonation reaction too. Examples of vitrimers based on carbonate exchange are very scarce,[230,231] and they rely on Ti(IV) catalysts, they thus exhibit similar flaws to metal-catalyzed transesterification vitrimers discussed earlier. Smart molecular design based on the knowledge on activating groups effects on transcarbonation might help the development of such transcarbonation vitrimers.

Dioxaborolane transesterification acceleration

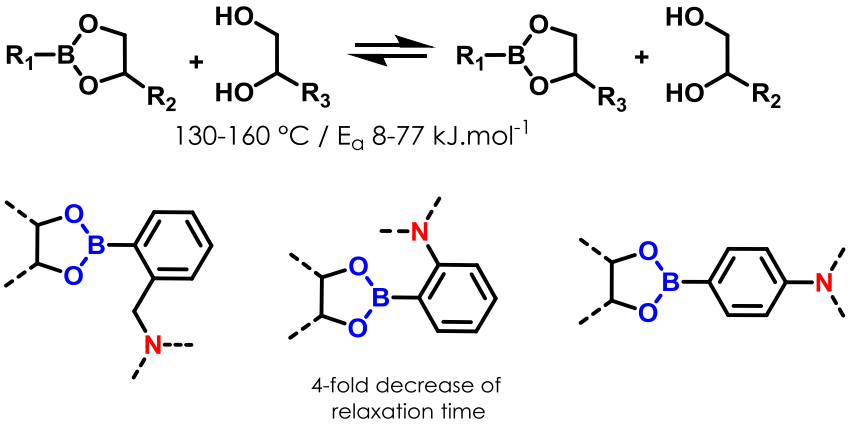


Figure 15. Reported activating groups enhancing dioxaborolanes exchange rate, range of stress-relaxation experiments temperatures[25] and activation energies.[24]

As discussed previously, boronic esters were mainly used in aqueous media. Therefore, the effects of activating groups on boronic esters were mainly described under such conditions. Although the behaviour of an exchangeable bond is very different in solution and in the bulk of a material, especially with a peculiar solvent such as water, it may still be possible to draw general conclusions on the effects of activating groups (Figure 15). In aqueous solution, there is an equilibrium between the dissociated boronic acid-diol couple and the corresponding boronic ester. The formation of a boronic ester by reaction between a boronic acid and a diol must be performed at a pH higher than the pKa of the acid.[232,233] Interestingly the pKa of boronic acids can easily be tuned by chemical modification. For instance, compared to the pKa value of 8.8 of phenylboronic acid, the pKa of methylboronic acid is 10.4 whereas the pKa of the very electron-withdrawing 3-pyridyl boronic acid is 4.0.[84] This shift of the esterification equilibrium gives a glimpse of the possible electronic and internal catalysis effects. An early study showed that arylboronic acids bearing *ortho*-neighboring groups containing oxygen, sulfur or fluorine do not enhance the esterification nor the transesterification.[234] Nevertheless, electron-withdrawing groups decrease boronic acid pKa whereas electron-donating groups increase it,[83,84] and destabilize the ester bond. For instance, the boron atom of phenylboronic acids are reported to be highly electron deficient, which reduces the pKa and facilitates ester formation.[84,233,235] Recently, benzoxaborole-crosslinked polyethylene glycol (PEG) networks were synthesized out of 4-carboxy-3-fluorophenylboronic acid along with its non-fluorinated counterpart (Figure 16). Four-arm amine-terminated PEG was modified with 4-carboxy-3-fluorophenylboronic acid or 4-carboxy-phenylboronic acid to afford tetrafunctional boronic acids. The same procedure was applied to d-glucolactone to obtain a tetrafunctional diol. Each tetrafunctional acid was then reacted with the tetrafunctional diol to make a network (Figure 16). This study showed that the resulting partially fluorinated material had a higher dynamic modulus and a faster relaxation time than the non-fluorinated analog.[236]

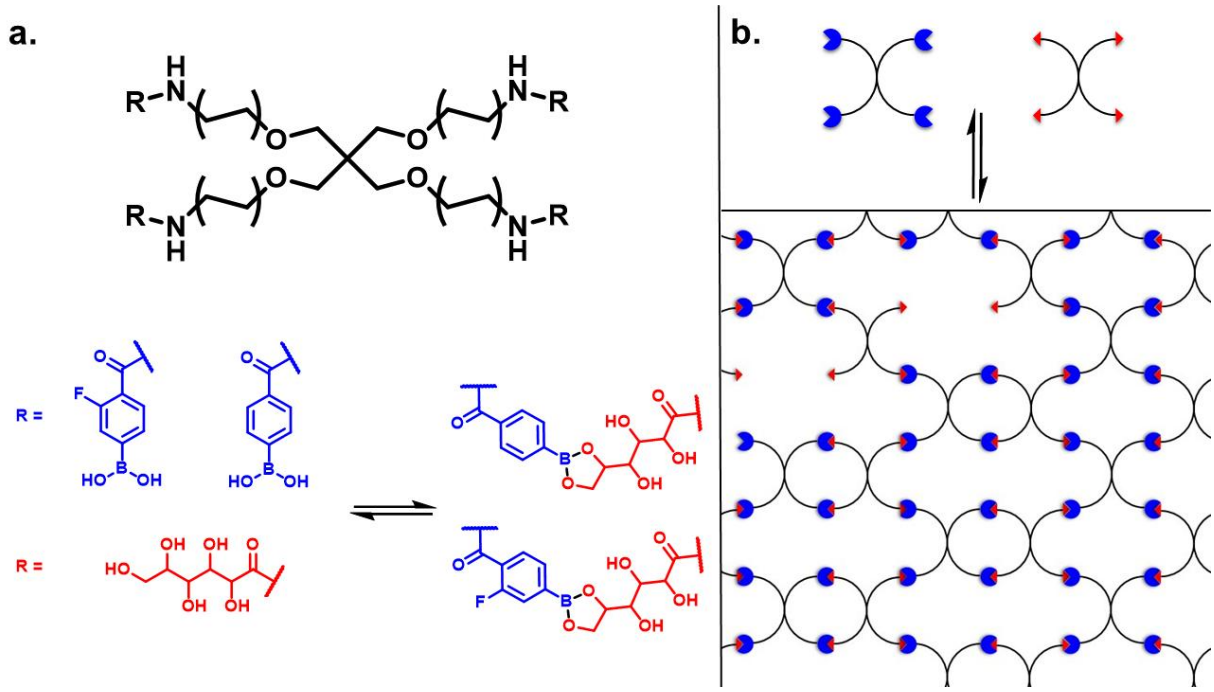


Figure 16. Synthesis of a network based on boronic esters a. polyethylene glycol (PEG) monomers functionalized by boronic acids (blue) and diols (red) and their equilibrium with the boronic ester form b. schematic representation of the network.[236]

Nevertheless, the most studied and most promising activating groups so far are nitrogen-containing groups. Aminomethyl-substituted arylboronic acids were shown to be esterified several orders of magnitude faster than non-substituted phenylboronic acids.[237] Their transesterification was also accelerated compared to unsubstituted boronic acids or such acids bearing substituents containing oxygen, sulfur or fluorine.[234,238] In solution the addition of a dimethylaminomethyl group on a phenylboronic ester was shown to accelerate the rate of transesterification by five orders of magnitude.[44] Amino group on the ortho or para position decreases the pKa of phenylboronic acid,[233] and facilitates the formation of ester.[239] This is due to electronic substituent effects on the aromatic ring. Even when the amino moiety is not directly attached to the aromatic ring, the acceleration effect is noticeable. In this case, the effect is caused by the formation of B-N dative bonds (a proper example of neighboring group participation, Figure 17a).[83,85,233,239]

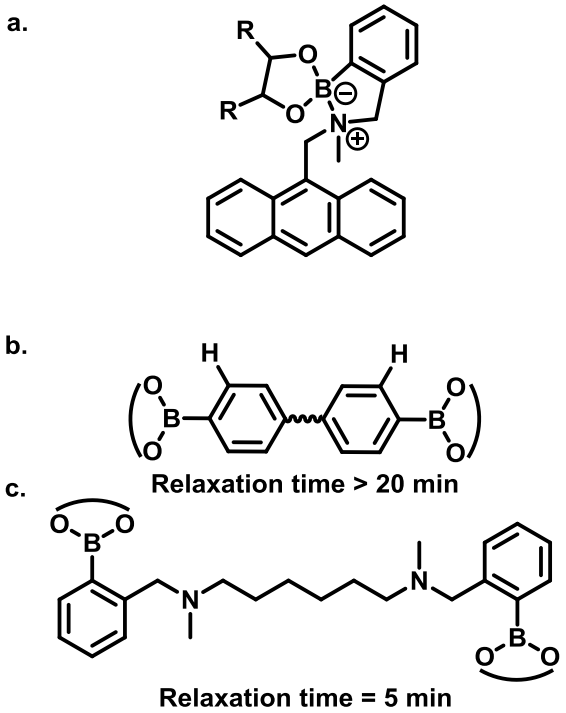


Figure 17. a. Example of coordinative B-N bond[239] b. Slow exchange crosslinker and c. fast exchange crosslinker (bottom) studied by Guan et al.[44]

Interestingly, amino activating groups have been implemented in vitrimers.[44] They demonstrated an accelerating effect on boronic esters transesterification in bulk, which enabled the tuning of the properties of dioxaborolane vitrimers. Indeed materials containing amino activating groups relaxed stress within 5 minutes while the reference dioxaborolane material required more than 20 minutes (Figures 17b and 18).

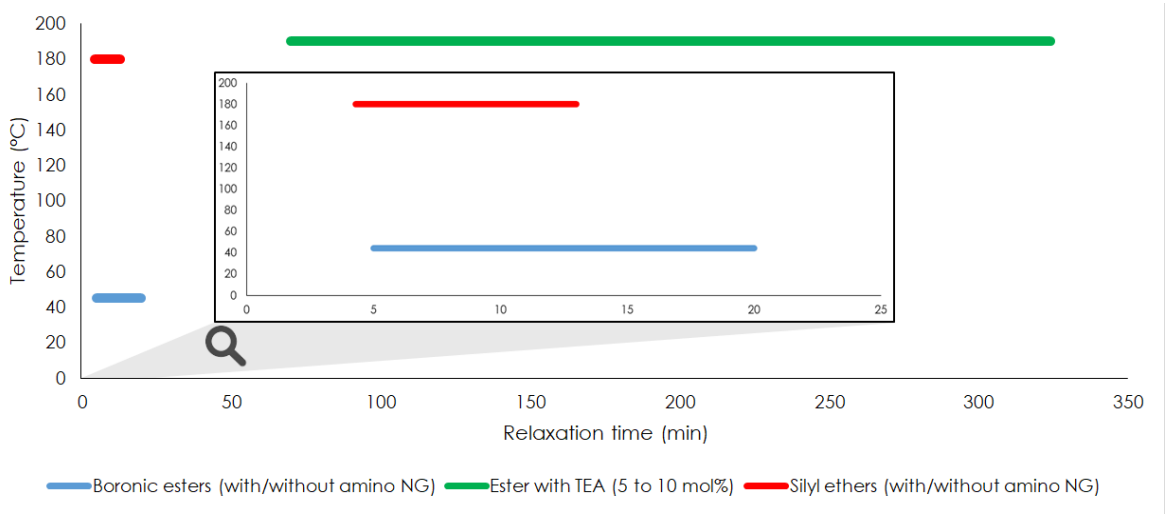


Figure 18. Effect of amine activating groups on the relaxation time of vitrimers with different kinds of exchangeable bonds (NG stands for neighbouring group and TEA for triethanolamine).

Other kinds of effects such as steric interactions and ring strain also play a role in the ester stability, as functional groups attached or adjacent to the boron atom on a boronic acid decrease the association constant with diols.[83,232,240] Steric hindrance is particularly relevant in polymers. Sumerlin et al. reported higher pKa and lower binding affinity of boronic acids-containing polymers compared to small molecules. The monomer pKa was 7.2 whereas the polymer had a pKa of 8.2. In the polymer,

the low mobility of the chains limited the availability of the binding sites.[87,232] Great care should be taken in the design of the exchangeable bond as the effect obtained can be opposite to the expected one in some cases. For instance, in a recent study, vitrimers based on nitrogen-coordinating cyclic boronic diesters were synthesized, with a dative B→N bond embedded in the cyclic diester (Figure 19).[241] This particular structure offered an improved resistance to hydrolysis, but also lowered the exchange rate compared to other cyclic boronic esters. In this particular case the effect on transesterification is somewhat counterintuitive. In summary, boronic esters in polymers allow the fine tuning of materials properties thanks to activating groups[84] with electronic and/or steric effects. This feature is interesting for vitrimers design. However, the knowledge on these effects in bulk remains scarce and deserves further investigations.[236]

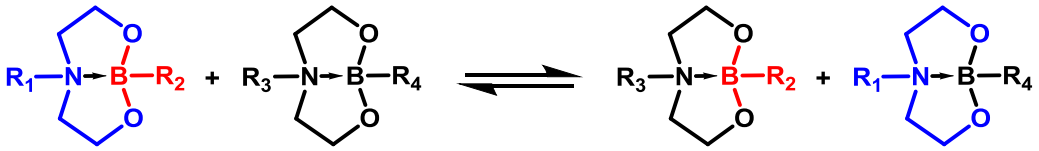


Figure 19. Nitrogen-coordinating cyclic boronic diester exchange[241]

Disulfides metathesis: effect of aromatic substituents

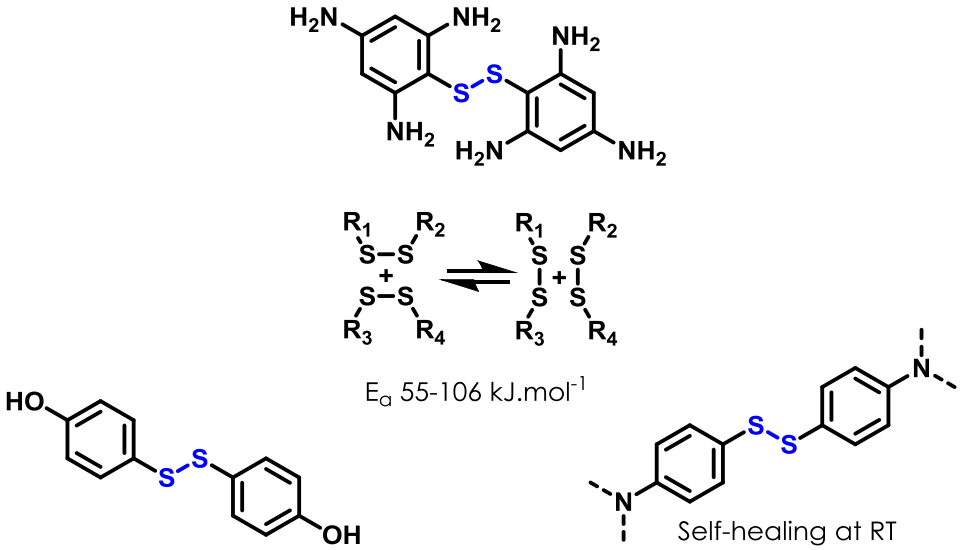
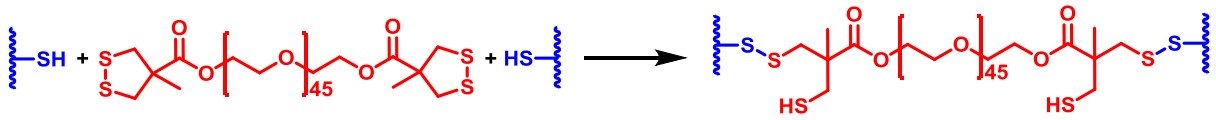


Figure 20. Disulfide exchange enhancement by activating groups (activation energy from Jourdain et al.[24]*).*

Neighboring group participation (NGP) in the exchange of disulfide bonds has hardly been probed yet, and the data readily available on this topic focus on the dissociative [2+1] radical assisted mechanism previously discussed in the "Disulfides" paragraph of Part II (Figure 20). However, this general knowledge on disulfide bonds strength is useful to understand how to tune their dynamic behaviour. Aromatic disulfides were mainly investigated, as the exchange reaction does not require the use of a catalyst to occur significantly contrary to exchange between alkyl disulfides usually catalysed by triethylamine or tributylphosphate for instance.[110-113,242,243] Alkyl disulfides metathesis is a very slow reaction and even considered as not spontaneous in the absence of a catalyst, especially in solid state.[115] Adding 6 % of triethylamine is however sufficient for the reaction to happen.[244] Phosphines are also good catalyst candidates and 5 mol% tricyclohexylphosphine was reported to accelerate the reaction 240 times in solution at room temperature, whereas the same amount of tri(dimethylamino)phosphine accelerated it 520 times, although some degradation products were

observed in that case.[245] Nevertheless a catalyst-free self-healable hydrogel based on alkyl disulfide was reported.[246] The network was formed by harnessing the thiol-disulfide exchange reaction of a telechelic thiol-ended PEG with telechelic PEG bearing cyclic five-membered disulfide (Scheme 29). This network formation did not require any catalyst, as the tension of the five-membered disulfide ring favors its opening and enhances the exchange reaction. This design also allowed self-healing in slightly acidic condition, whereas such behavior is usually observed only in neutral and alkaline mediums, in the presence of nucleophilic thiolates.



Scheme 29. Hydrogel polymerization by thiol-disulfide exchange on strained five-membered ring disulfides[246]

Nitrogen has an enhancing effect[110] in different kinds of activating groups such as tertiary amines on phenyl disulfides,[111,247] thiuram disulfides[248] or sulfenamides.[243] For instance aromatic sulfenamide-derived disulfides (Figure 21) exhibited a bond dissociation energy (BDE) of around 35 kcal.mol^{-1} whereas their nitrogen-free counterpart exhibited a BDE around 50 kcal.mol^{-1}.[243] The lower is the BDE, the more radicals are generated, and the easier is the exchange reaction. Thanks to the enhancement of the exchange reaction, some catalyst-free materials based on aromatic disulfides exhibited self-healing at room temperature.[116] In those materials bis(4-aminophenyl)disulfides were used as dynamic crosslinkers to make poly(urethane-urea) systems.

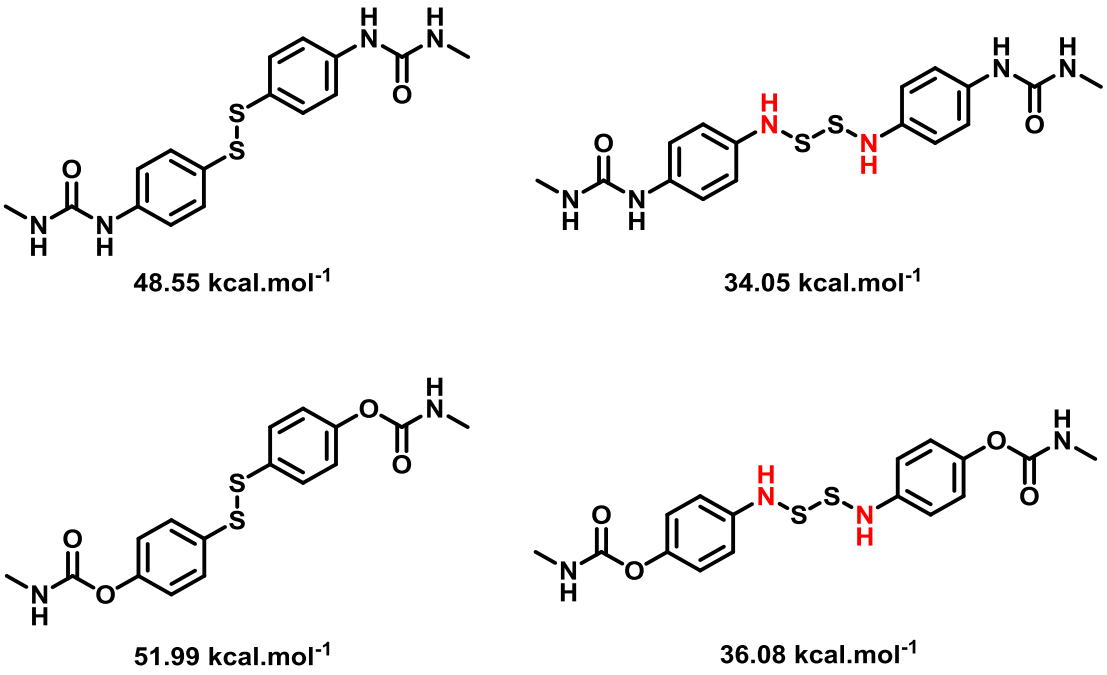


Figure 21. Structure of aromatic sulfenamide-derived disulfides, and the associated bond dissociation energies (BDE) calculated by DFT.[243]

4-hydroxyphenyl disulfides are known to undergo faster radical generation than their 4-aminophenyl homologs[113] but this effect is still poorly documented. 4-hydroxyphenyl disulfide exchange reaction with diphenyl disulfide reached 60 % conversion in only 2 h whereas 12 h were necessary for the 4-aminophenyl disulfide with diphenyl disulfide under UV radiation. Matxain et al. published a thorough theoretical reactivity study on disulfide bonds dissociation energy.[110] They pointed out that electron donating groups lower the energy of the dissociation and reversely electron withdrawing

groups (EWG) increase it. Compared to the 48 kcal.mol^{-1} BDE value of unsubstituted aromatic disulfides, *p*-sulfonic acid substituent increased this value to 55.6 kcal.mol^{-1} whereas an amino derivative in *para* position decreased the BDE to 41.3 and even to 30.1 kcal.mol^{-1} with the trisubstituted bis(2,4,6-triaminephenyl) disulfide (Figure 22a). They also reported that dendralene and thiuram disulfides (Figure 22b and 22c) have low BDE, which may allow self-healing at room temperature and provide a good alternative to aryldisulfides. Though disulfide bonds have been known for a long time, there is still much research needed to understand how to better tune the exchange reaction in materials, especially in the case of the associative thiol-disulfide reaction about which literature remains scarce.

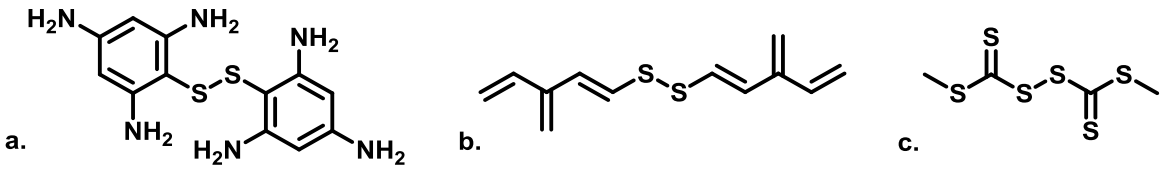


Figure 22. Structures of a. bis(2,4,6-triaminephenyl) disulfide b. dendralene disulfide c. thiuram disulfide.

Internal catalysis of silyl ether transalkoxylation by amines, urethanes and ureas

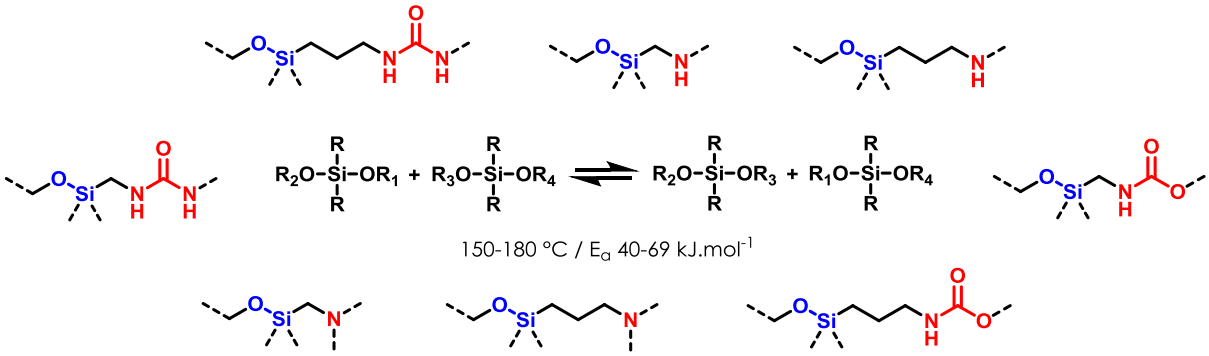


Figure 23. Examples of activating groups enhancing silyl ether exchange and range of stress-relaxation experiments temperature[25] and activation energies.[24]

When implementing the previously discussed ion pair dissociation-triggered mechanism in silyl ethers, the main parameters to tune the exchange reactivity are obviously the nature[131] and concentration[130] of the ion pairs. The environment of the counterion influences its ability to dissociate and thus the rate of the exchange reaction (Figure 23). For instance, cation complexation by oxygen atoms on neighboring siloxane chains was reported to increase the electrophilic behavior of silicon atoms and the nucleophilic behavior of silanolate moieties, facilitating trans-siloxanation.[131] In 1970, Wright et al. studied the equilibrium between chains and rings in $[R(CH_3)SiO]_x$ structures, showing that, for x=2 or 4, bulkier R led to favored cyclization. However, the opposite effect was shown for x>10.[249] Catalysis by triphenylphosphine (TPP) and triazabicyclodecene (TBD) in silicone materials was also reported. TPP led to materials with a temperature of plastic flow around 240 °C whereas the materials containing TBD flowed at 120 °C.[250] In 2014, tertiary and secondary amines, urea and carbamate groups on α- and γ-silanes (Figure 24) were reported to interact with the alkoxy leaving group or the attacking nucleophile thus increasing the hydrolysis rate of the alkoxy group. This study carried out both in solution and *in silico* showed the significant influence of several activating groups. For instance, secondary amines accelerated the hydrolysis reaction from 5 to 50 times and tertiary amines at least 40 times. Carbamate groups accelerated the reaction from 6 to 80 times, depending on their position and structure.[251]

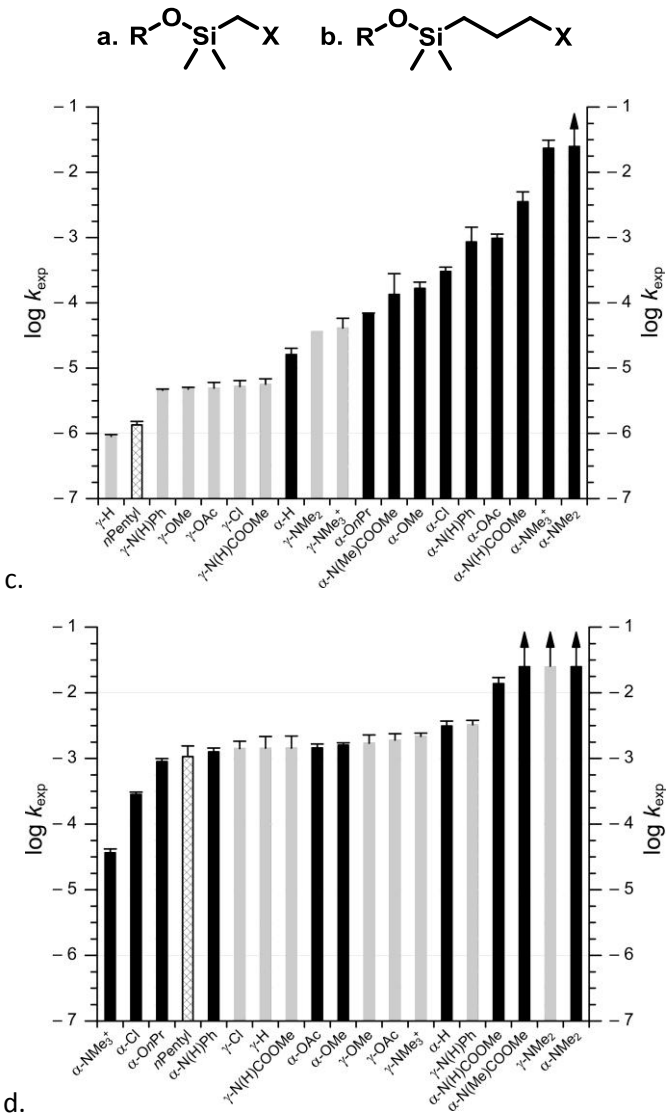
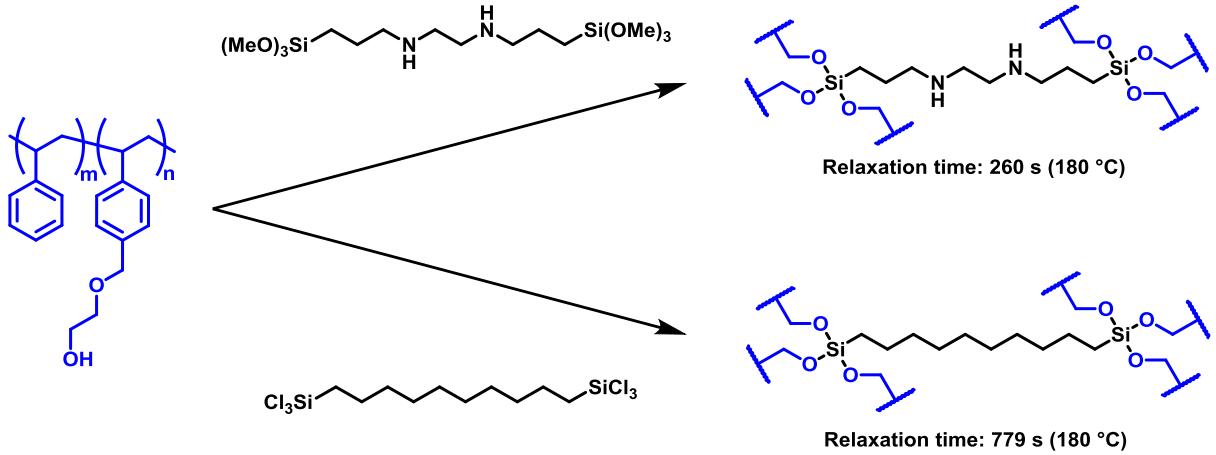


Figure 24. Structure of a. α-silanes and b. γ-silanes. The effects of various -X substituents on the hydrolysis rate of the alkoxy group were studied c. in basic conditions and d. in acidic conditions.[251]

This result was later successfully implemented in malleable materials with activating amino moieties accelerating the exchange rate of silyl ethers.[45,252] A copolymer of styrene and 2-((4-vinylbenzyl)oxy)ethan-1-ol was synthesized by free radical copolymerization. Then the resulting copolymer was crosslinked either with *N*,*N*'-bis(3-(trimethoxysilyl)propyl)ethane-1,2-diamine or with 1,10-bis(trichlorosilyl)decane (Scheme 30). Both crosslinked structures were similar and the crosslinkers used had the same length. The relaxation time for the structure incorporating secondary amines was 260 s at 180 °C, three times less than the 779 s needed for the amine-free structure (Scheme 30).[45] Variations of the silyl ether bulkiness and the polymer backbone are suggested to tune the properties of these materials.[132]



Scheme 30. Synthesis of styrene-derived networks crosslinked by silyl ethers. Two crosslinkers were used, one bearing secondary amines (top), the other not (bottom). The reprocessability of the obtained materials was compared.[45]

The case of urethanes and hydroxyurethanes

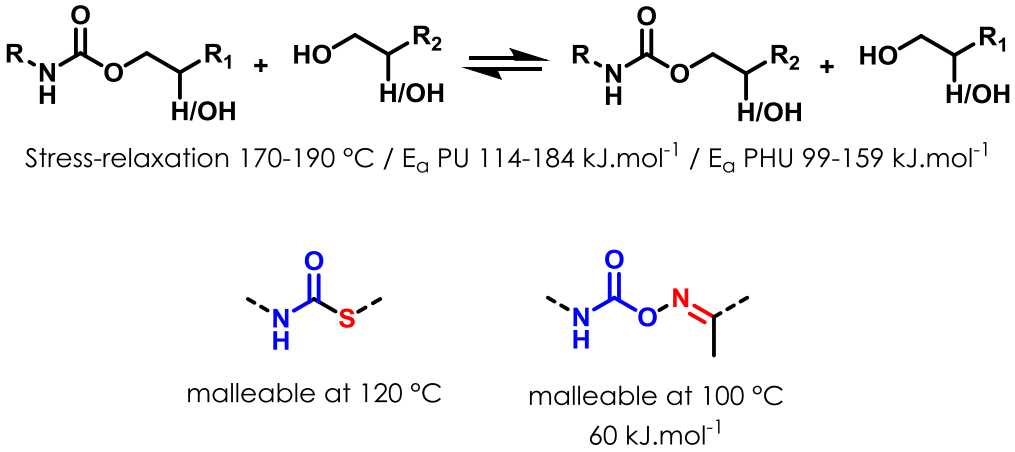


Figure 25. Characteristics of polyurethanes, polyhydroxyurethanes, polythiourethanes and poly(oxime-urethanes): range of stress-relaxation experiments temperatures[25] *or reprocessing temperatures and activation energies.*[24,253]

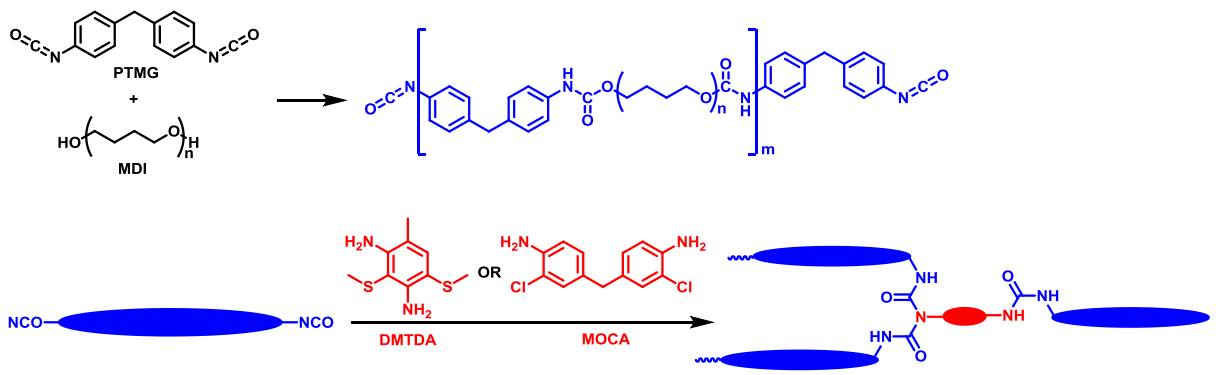
As discussed previously, the mechanism involved in polyhydroxyurethane exchange reaction remains uncertain. Hence, the determination of the effects of activating groups on transcarbamoylation is intricate as they were mainly studied for the dissociative decomposition reaction discussed in Part I (Figure 25).[254-256] It should be mentioned that an important activation reported is the oxime-promoted transcarbamoylation, similar to the effect on esters previously discussed. It was implemented in dissociative covalent adaptable networks since the mechanism is purely dissociative in this case.[253]

For thiourethanes solvolysis by thiols, secondary amines or alcohols suggested the reaction pathway was an associative addition/elimination mechanism[257] instead of the dissociative elimination/addition commonly accepted. Nonetheless, as previously pointed out, the recent implementation of thiourethane bonds in materials highlighted a dual associative and dissociative mechanism.[258] Knowledge on the effects of activating groups on hydroxyurethane-based vitrimers is very limited. Nevertheless an excess of free exchanging dangling groups, namely alcohol groups for polyurethanes and thiol groups for polythiourethanes were shown to favour the associative pathway

and decrease degradation reactions. Furthermore, this excess of dangling exchanging groups allows a better control over the reprocessing temperature and shorter reprocessing time.[144,258] After 70 mins at 140 °C a PU network without free –OH group exhibited 83 % recovery of crosslink density in the presence of 1 mol% dibutyltindilaurate (DBTDL) as catalyst. In contrast, only 15 mins at 120 °C were sufficient to reprocess a PU containing 20 % of free -OH.[258] In contrast, an increase of the relaxation time was observed in the case of thiourethane-based networks (Scheme 11) containing free thiols compared to the thiol-free analog. This counterintuitive result was explained by a change from a dissociative to a slower associative mechanism.[144] In conclusion, the chemistry of polyhydroxyurethanes is much more complex that it seems at first glance. Dissociative and associative exchange mechanisms compete and are influenced by many parameters such as the availability of exchangeable group, the presence of activating group or internal catalysts, or the temperature. Therefore, much caution should be taken when designing covalent adaptable networks out of polyhydroxyurethanes.

Ureas exchange

Recently a polyurethane-urea elastomer was claimed to be a vitrimer.[259] The authors first synthesized a PU prepolymer out of poly(oxatetramethylene) glycol (PTMG) and 4,4'-diphenylmethane diisocyanate (MDI). Then this prepolymer was mixed either with 3,5-dimethylthio-2,4-toluenediamine (DMTDA) or with 3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA) to form exchangeable biuret groups (*N*,*N*'-diaryl urea) (Scheme 31). Because the diamines used are primary, each amine is able to react twice thus ensuring the formation of a crosslinked materials (primary diamines can be considered as hidden tetrafunctional reactants). The amines used bore either electron-donating methylthio substituents or electron-withdrawing chlorine atoms. The stress relaxation time of the methylthio groups-containing network was 3 to 4 times shorter than that of the chlorinated analog, depending on the temperature (100 to 120 °C). The relaxation was assigned to urea-urea exchanges and the mechanism was reported as associative.[259] Nevertheless there are little proofs to support this claim.



Scheme 31. Synthesis of polyurethane-urea self-healable elastomers.[259]

Transimination acceleration by activating groups

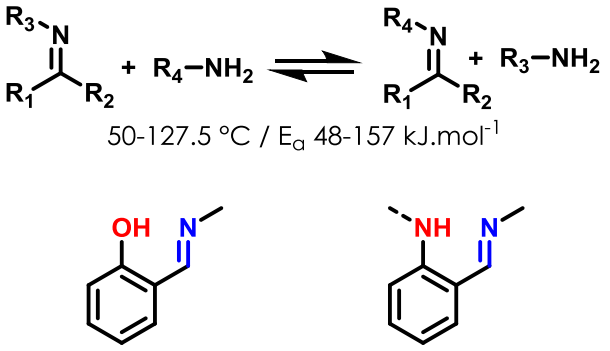
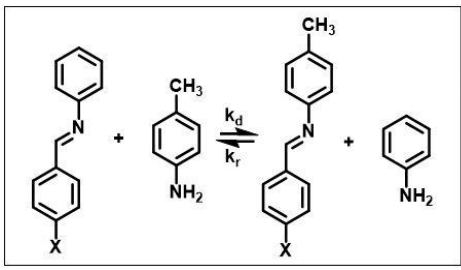


Figure 26. Characteristics of transimination: reported range of stress-relaxation experiments temperatures[25] and activation energies.[260] Two examples of potentially active neighboring groups are given.

The success of imines-derived vitrimers (Figure 26) may be explained by the versatility of this linkage, but also because these vitrimers can be reprocessed without the need for a catalyst.[163-174] When used in organic chemistry or biochemistry, transimination was reported to be catalysed by thiourea metal complexes (2 orders of magnitude rate acceleration),[177] triflate salts of scandium, terbium, samarium and other lanthanides (up to 5 orders of magnitude acceleration),[178,261] zinc bromide,[262] iron chloride, copper chloride and magnesium chloride.[263] Besides, acid and basic catalysis are known to be efficient as well, in aqueous[175,264] or organic solutions.[175,265] In particular, interesting examples of internal basic catalysis in solution were reported in the 1980s, using primary amines featuring an internal tertiary amine function.[264,265] Ciaccia et al.[180] reported a study on aromatic imines in organic solvents at room temperature. Part of this work dealt with the exchange between *N*-benzylideneanilines and p-toluidine (Figure 27). The exchange reaction exhibited low equilibrium constants (K_{eq}<10), thus the results could have been carefully extrapolated to degenerate system such as those encountered in vitrimers. The authors showed that the rate of the forward transimination reaction was almost unaffected by EWG and EDG on the imine aromatic ring, but that the reverse reaction was mildly affected by these substituents. Electron-donating $–OCH_3$ group slightly increased the reverse reaction rate, whereas electron-withdrawing -CN and $-NO_2$ groups decreased this rate (Figure 27). Similarly, Schaufelberger et al.[262] studied the impact of substituents on the exchange of aromatic imines with benzyl amines in the presence of zinc bromide as catalyst in acetonitrile. Nevertheless, in this system, two simultaneous reactions were involved, imine isomerization and transimination. Thus, it would be dubious to draw general conclusions on internal catalysis based on this study.

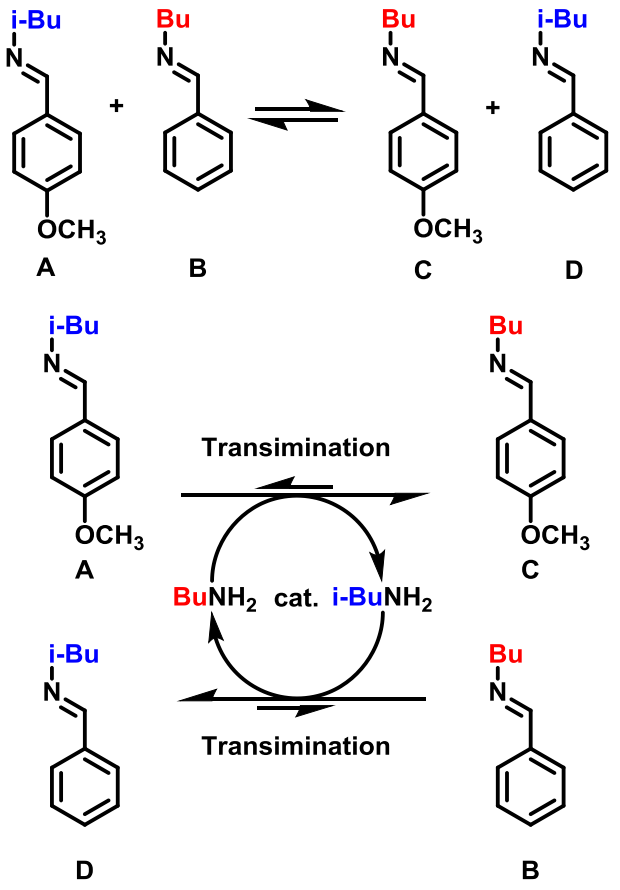


X	K	k_d ($M^{-1}s^{-1}$)	k_r ($M^{-1}s^{-1}$)
H	2.6	1.0×10^{-1}	3.8×10^{-2}
OCH_3	3.0	1.2×10^{-1}	4.0×10^{-2}
CN	4.5	1.1×10^{-1}	2.4×10^{-2}
NO_2	7.2	0.94×10^{-1}	1.3×10^{-2}

Figure 27. Transimination reaction between N-benzylideneanilines and p-toluidine, and kinetic parameters studied by Ciaccia et al.[180]

Since the first step of the amine-imine exchange reaction is associative, it occurs at room temperature without catalyst in solvents only with unhindered reactants.[179] This idea underlines the fact that the environment of the exchangeable bond likely plays a major role in the reaction. For instance the solvent used to make dynamic covalent gels had an influence, acetonitrile allowing

faster imine exchange than toluene.[266] Additionally imine metathesis is catalysed by zirconium, molybdenum, rhenium and niobium in organic solvents if the temperature reaches 100 °C[179] and by hafnium imido complexes at 80 °C as well.[267] An interesting strategy involving minute amounts of primary amines was also reported to accelerate this reaction in solution at room temperature.[179] The effect of primary amines on imine metathesis was investigated in terms of mechanism and thermodynamics. Mechanistically speaking the overall reaction can be seen as two concomitant transimination reactions (Scheme 32). Thus, it is not *stricto sensu* an imine metathesis, but the overall result is the same. Minute amounts of an imine A bearing an isobutyl group exchange with the minute amount of n-butylamine leading to the release of minute amounts of the exchanged imine C and isobutylamine. This amine then undergoes transimination with an imine B bearing a n-butyl group. This second step releases the exchanged imine D and n-butylamine able to react with A, and so on. The overall reaction is an equilibrium between amines A and B on one hand, C and D on the other. Thermodynamically speaking the overall reaction is an imine metathesis.[179] This effect was implemented in imine-crosslinked PEG networks. A slight excess of dangling primary amines enabled self-healing at 50 °C within 5 min.[266] Thus choosing carefully the stoichiometry for the synthesis of imine-derived vitrimers would enable the tuning of their properties.

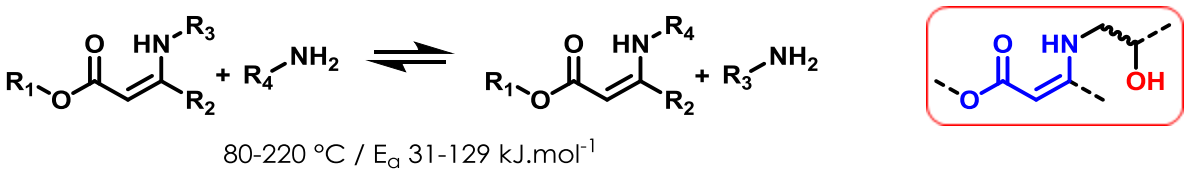


Scheme 32. Imine metathesis catalysis by minute amounts of primary amines.[179]

Recently the effect of hydrogen bonds was also emphasized. Indeed hydrogen bond donors such as thioureas and squaramides catalysed both imine metathesis and transimination in solution and their efficiencies depended on their structures.[268] Similarly imines derived from salicylaldehyde were reported to be stabilized by hydrogen bonding with -OH or –NHR substituents on the ortho

position.[269] Once again, this effect could be used in the molecular design of imines to tune the exchangeable bond properties.

Vinylogous urethanes and amides, an efficient exchange chemistry without catalyst



Scheme 33. Characteristics of vinylogous urethane transamination: reported range of stress-relaxation experiments temperatures[25] and activation energies.[24] Dangling hydroxyl groups accelerates the relaxation time of VU materials.

Transamination of vinylogous urethane is a very effective exchange reaction and enables chemists to design easily-reprocessable catalyst-free vitrimers (Schemes 16 and 33). This observation might be the cause for the rarity of reports on such effects on vinylogous urethanes. Although the exchange is so efficient that many catalyst-free vitrimers were synthesized, vinylogous urethane-based CANs would still benefit from activating group participation or internal catalysis to lower reprocessing temperatures. Actually, an example of internal catalysis was recently reported in vinylogous urethane-crosslinked epoxy-amine materials.[199] Tri- and di-functional amines were reacted with a bisacetoacetate to prepare a vinylogous urethane bond-containing hardener for an industrial epoxy resin. Two synthesis methods were compared. On the one hand, the amines, the bisacetoacetate and the epoxy resin were mixed in one-pot. On the other, the amines and the bisacetoacetate reacted in a first step to yield a vinylogous urethane curing agent bearing free primary amines. Then the curing agent was mixed with the epoxy resin in a second step (Figure 28). The difference lies in the water release when amines and the bisacetoacetate reacted together. In the one-pot strategy, this water was trapped in the material, whereas in the two-step strategy the water produced during the first step was removed prior to the second step, to yield a water-free material. The materials exhibited a relaxation time at 160 °C of 3.5 s for the one-pot material and of 5.5 s for the two-step synthesis, showing no significant difference between the two preparation procedures. These values must be compared with the 25.5 s relaxation time observed in epoxy-free vinylogous urethanes vitrimers with a similar structure, although having a higher vinylogous urethane bond concentration. Certainly, the network structure influences the relaxation time, and thus direct comparison of these values might be adventurous, but an internal catalytic effect from the dangling hydroxyl groups is likely responsible for the shorter relaxation times.[199] To support this idea the authors performed model reaction on small molecules. They studied the disappearance of propyl-3-(octylamino)but-2-enoate (octyl VU) with benzylamine in 2-hexanol or dodecane at 100 °C. The reaction was faster in 2-hexanol, showing the accelerating effect of hydroxyl moieties on the exchange reaction, independently of any matrix effect. As the study of vinylogous urethane vitrimers is popular, numerous tuning possibilities might emerge in the future, by implementation of internal catalysis in these networks, but also by variation of the backbones nature and length.

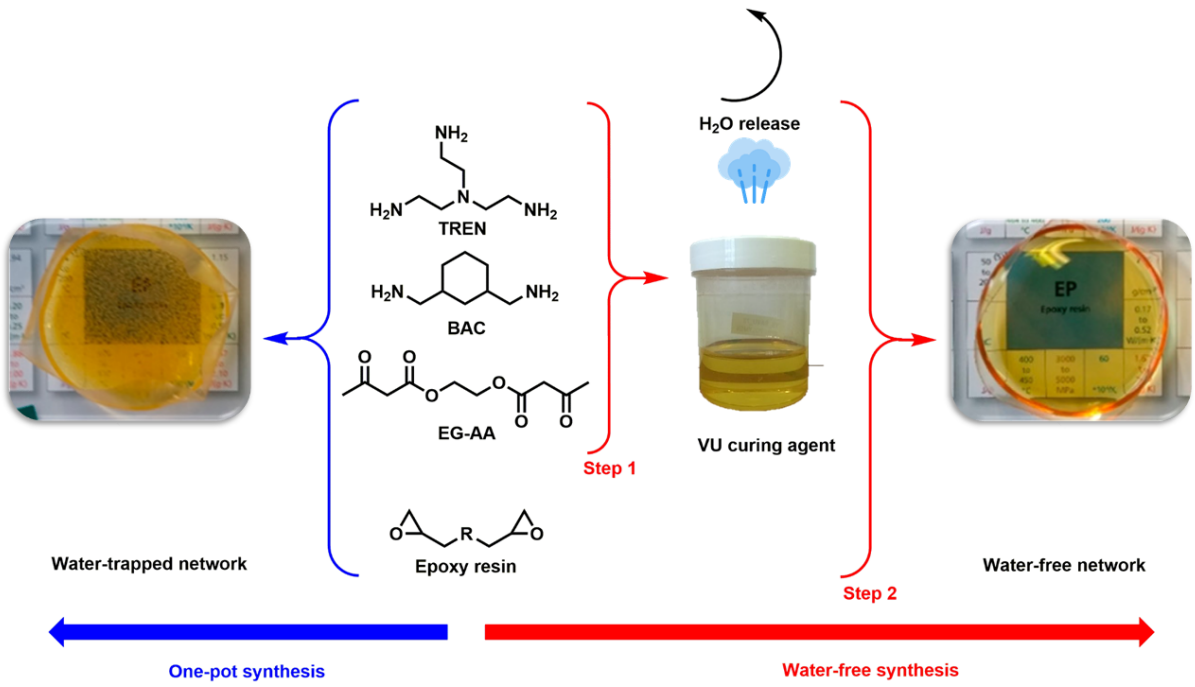


Figure 28. Two strategies to synthesize VU networks were reported by Spiesschaert et al.[199] The one-pot strategy traps the water released by the reaction. Yhe two-step strategy allows to remove water from the VU curing agent after the first step, allowing water-free network. TREN = tris(2-aminoethyl)amine; BAC = 1,3-bis(aminomethyl)cyclohexane; EG-AA = ethylene glycol–bisacetoacetate.

Hints for diketoenamines activation

As previously mentioned, diketoenamines were essentially studied as protecting groups and there is no extensive knowledge on a potential effect of neighboring groups. Nevertheless, in the work of Augustyns et al.[201] already discussed earlier, a few interesting trends on reactivity were gathered. The two amino groups on lysine did not have the same reactivity toward the exchange of Dde group. Unprotected ε-NH_2 groups could exchange with protected ε-NH_2 and α-NH_2 groups but free α-NH_2 groups could not exchange Dde with ε-NH_2. This was probably because α-NH_2 groups were too sterically hindered and not nucleophilic enough due to the neighboring electron-withdrawing carboxylic acid. In addition, when 2-acetyldimedone was reacted with polyamine, primary amines were selectively protected.[201] The use of diketoenamines in vitrimers is just starting to emerge and there is undoubtedly a lot to discover on this chemistry, based on the encouraging proof of concept recently disclosed.[204,205]

Effect of the alkylating agent on trialkylsulfonium salts exchange

As mentioned before, the knowledge on trialkylsulfonium exchange with thioethers is poor except for the proof-of-concept disclosed by Du Prez's group.[40] Of course, the most obvious parameters to tune the material reprocessability are the nature and quantity of the alkylating agent. Without alkylating agent, no stress relaxation was observed in polythioether.[40] Conversely increasing the concentration of the butyl brosylate alkylating agent from 1 to 10 mol% decreased relaxation time at 150 °C from 75 to 10 mins.[40] The same behaviour was observed using trimethylsulfonium iodide as alkylating agent.[124] Once again, there might be room for internal catalysis studies with this kind of chemistry. Indeed, this exchange reaction was studied on small arylalkylsulfides in solution. If no change in the kinetics was observed with electron-rich aromatic groups, electron-poor aromatic groups slowed down the conversion rate. The alkyl substituent bulkiness also played a role. Phenylalkyl sulfides bearing various alkyl groups were transalkylated with methyl iodide. *Tert*-butyl-phenyl sulfides reached full conversion in 25 hours whereas the butyl-, 3-pentyl- and 2,2-

dimethylpropyl- analogs only reached 70, 60 and 8 % conversion respectively. Diphenylsulfide showed no conversion at all.[270] This effect has never been studied in materials but underlines the importance of the exchangeable group and might bring useful insights. These articles also underline the effect of the counteranions which nucleophilicity likely plays a role as seen in the transalkylation of triazolium salts.[271-273]

Conclusion and outlook

Since the invention of vitrimers ten years ago, this class of organic materials has triggered an undeniable enthusiasm in the polymer scientists' community. These materials have not only aroused scientists curiosity, but their implications for industrial applications are also potentially transformative. Indeed the rheological behaviour of these materials allows a precise control of the viscosity upon heating. This property is central to processing and reprocessing issues. One drawback of these materials is that many vitrimers require catalysts, sometimes at high loadings, which raise concerns for the risks of leaching and premature ageing of the materials. Consequently, further work on vitrimers will likely focus on designing catalyst-free vitrimers and on the tuning of the vitrimers properties, especially the reshaping ability, for the associative systems already known. Parameters such as the crosslinking density, the concentration and availability of exchanging moieties, or the structure and chemical groups of the backbone are already known to influence the behaviour of vitrimers. A few studies on the effect of activating groups on the exchange reactions and consequently on materials reshaping are already available. Nonetheless, the use of this strategy to tune the rheologic profile of associative CANs is still in infancy. Beyond the sole tuning of the reshaping parameters, the study of activating group and internal catalysis would be a significant progress for understanding how the exchange reactions in vitrimers works, and it would give access to the scientist community to more intimate knowledge of this innovative class of polymer materials. At the moment knowledge on the phenomena occurring at the molecular scale in vitrimers is still poor. In addition, the mechanistic studies on the exchange mechanisms involved are sometimes only preliminary, or even inexistent. Moreover, activating groups can have an influence on the exchange mechanism at work in CANs. They may change an associative exchange into a dissociative one. Mechanistic studies are thus fundamental for the development of CANs. A better comprehension of the phenomena at the molecular scale would indeed allow scientists to design materials with original properties by exploiting such mechanism changes. Broadening the pool of techniques used to characterize CANs would also undoubtedly help to understand their behaviour, and contribute to a better and more purposeful design. For example, molecular mobility studies using dielectric spectroscopy or dynamic mechanical analysis could enrich the comprehension of these fascinating materials.

Funding: This work was funded by the Institut Carnot Chimie Balard CIRIMAT (16CARN000801)

References

1. Montarnal, D., Capelot, M., Tournilhac, F. & Leibler, L. Silica-like malleable materials from permanent organic networks. *Science (80-.).* **334**, 965–968 (2011).

2. Pascault, J.-P., Sautereau, H., Verdu, J. & Williams, R. J. J. J. *Thermosetting Polymers*; Marcel Dekker, Inc.: New York, 2002.

3. *Thermal Characterization of Polymeric Materials*; Tori, E. A., Ed.; Academic Press Inc.: New York, 1981.

4. Craven, J. M. U.S. Patent 3,435,003, 1969.

5. Bowman, C., Du Prez, F. & Kalow, J. Introduction to chemistry for covalent adaptable networks. *Polym. Chem* **11**, 5295-5296 (2020).

6. Kloxin, C. J., Scott, T. F., Adzima, B. J. & Bowman, C. N. *Covalent adaptable networks (CANs): A unique paradigm in cross-linked polymers*. *Macromolecules* **43**, 2643–2653 (2010).

7. Chujo, Y., Sada, K. & Saegusa, T. Reversible Gelation of Polyoxazoline by Means of Diels-Alder Reaction. *Macromolecules* **23**, 2636-2641 (1990).

8. Goussé, C., Gandini, A. & Hodge, P. Application of the Diels-Alder reaction to polymers bearing furan moieties. 2. Diels-Alder and retro-Diels-Alder reactions involving furan rings in some styrene copolymers. *Macromolecules* **31**, 314–321 (1998).

9. Jones, J. R., Liotta, C. L., Collard, D. M. & Schiraldi, D. A. Cross-linking and modification of poly(ethylene terephthalate-co-2,6-anthracenedicarboxylate) by Diels-Alder reactions with maleimides. *Macromolecules* **32**, 5786–5792 (1999).

10. Imai, Y., Itoh, H., Naka, K. & Chujo, Y. Thermally reversible IPN organic-inorganic polymer hybrids utilizing the Diels-Alder reaction. *Macromolecules* **33**, 4343–4346 (2000).

11. McElhanon, J. R. & Wheeler, D. R. Thermally responsive dendrons and dendrimers based on reversible furan-maleimide diels-alder adducts. *Org. Lett.* **3**, 2681–2683 (2001).

12. Chen, X., Dam, M. A., Ono, K., Mal, A., Shen, H., Nutt, S. R., Sheran, K., Wudl, F. A thermally re-mendable cross-linked polymeric material. *Science (80-.).* **295**, 1698–1702 (2002).

13. Oehlenschlaeger, K. K., Mueller, J. O., Brandt, J., Hilf, S., Lederer, A., Wilhelm, M., Graf, R., Coote, M. L., Schmidt, F. G., Barner-Kowollik, C. Adaptable hetero Diels-Alder networks for fast self-healing under mild conditions. *Adv. Mater.* **26**, 3561–3566 (2014).

14. Scott, T. F., Schneider, A. D., Cook, W. D. & Bowman, C. N. Chemistry: Photoinduced plasticity in cross-linked polymers. *Science (80-.).* **308**, 1615–1617 (2005).

15. Breuillac, A., Kassalias, A. & Nicolaÿ, R. Polybutadiene Vitrimers Based on Dioxaborolane Chemistry and Dual Networks with Static and Dynamic Cross-links. *Macromolecules* **52**, 7102–7113 (2019).

16. Taplan, C., Guerre, M., Winne, J. M. & Du Prez, F. E. Fast processing of highly crosslinked, low-viscosity vitrimers. *Mater. Horizons* **7**, 104–110 (2020).17. Capelot, M., Unterlass, M. M., Tournilhac, F. & Leibler, L. Catalytic control of the vitrimer glass transition. *ACS Macro Lett.* **1**, 789–792 (2012).

18. Denissen, W., Rivero, G., Nicolaÿ, R., Leibler, L., Winne, J. M., Du Prez, F. E. Vinylogous Urethane Vitrimers. *Adv. Funct. Mater.* **25**, 2451–2457 (2015).

19. Denissen, W., Winne, J. M. & Du Prez, F. E. Vitrimers: Permanent organic networks with glass-like fluidity. *Chemical Science* **7**, 30–38 (2016). 20. Obadia, M. M., Jourdain, A., Cassagnau, P., Montarnal, D. & Drockenmuller, E. Tuning the Viscosity Profile of Ionic Vitrimers Incorporating 1,2,3-Triazolium Cross-Links. Adv. Funct. Mater. **27**, 1703258 (2017).

21. Chakma, P., Morley, C. N., Sparks, J. L. & Konkolewicz, D. Exploring How Vitrimer-like Properties Can Be Achieved from Dissociative Exchange in Anilinium Salts. *Macromolecules* **53**, 1233–1244 (2020).

22. Hayashi, M. Implantation of Recyclability and Healability into Cross-Linked Commercial Polymers by Applying the Vitrimer Concept. Polymers **12**, 1322 (2020).

23. Hayashi, M. & Chen, L. Functionalization of triblock copolymer elastomers by cross-linking the end blocks: via trans-N -alkylation-based exchangeable bonds. Polym. Chem. **11**, 1713–1719 (2020).24. Jourdain, A., Asbai, R., Anaya, O., Chehimi, M. M., Drockenmuller, 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* **53**, 1884–1900 (2020).25. Elling, B. R. & Dichtel, W. R. Reprocessable Cross-Linked Polymer Networks: Are Associative Exchange Mechanisms Desirable? *ACS Cent. Sci.* **14**, 53 (2020).

26. Zhang, L. & Rowan, S. J. Effect of Sterics and Degree of Cross-Linking on the Mechanical Properties of Dynamic Poly(alkylurea−urethane) Networks. *Macromolecules* **50**, 5051−5060 (2017).

27. Imbernon, L., Norvez, S. & Leibler, L. Stress Relaxation and Self-Adhesion of Rubbers with Exchangeable Links. *Macromolecules* **49**, 2172–2178 (2016).

28. Alabiso, W. & Schlögl, S. The impact of vitrimers on the industry of the future: Chemistry, properties and sustainable forward-looking applications. *Polymers* **12**, 1660 (2020).

29. Liu, T., Zhao, B. & Zhang, J. Recent development of repairable, malleable and recyclable thermosetting polymers through dynamic transesterification. *Polymer.* **194**, 122392 (2020).

30. Yang, X., Guo, L., Xu, X., Shang, S. & Liu, H. A fully bio-based epoxy vitrimer: Self-healing, triple-shape memory and reprocessing triggered by dynamic covalent bond exchange. *Mater. Des.* **186**, (2020).

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

32.

33.

34.

35. Altuna, F. I., Pettarin, V. & Williams, R. J. J. Self-healable polymer networks based on the cross-linking of epoxidised soybean oil by an aqueous citric acid solution. *Green Chem.* **15**, 3360–3366 (2013).

36. Han, J., Liu, T., Hao, C., Zhang, S., Guo, B., Zhang, J. A Catalyst-Free Epoxy Vitrimer System Based on Multifunctional Hyperbranched Polymer. *Macromolecules* **51**, 6789–6799 (2018).

37. Liu, T., Zhang, S., Hao, C., Verdi, C., Liu, W., Liu, H., Zhang, J. Glycerol Induced Catalyst-Free Curing of Epoxy and Vitrimer Preparation. *Macromol. Rapid Commun.* **40**, 1800889 (2019).

38. Altuna, F. I., Hoppe, C. E. & Williams, R. J. J. Epoxy vitrimers with a covalently bonded tertiary amine as catalyst of the transesterification reaction. *Eur. Polym. J.* **113**, 297–304 (2019).

39. Guerre, M., Taplan, C., Nicolaÿ, R., Winne, J. M. & Du Prez, F. E. Fluorinated Vitrimer Elastomers with a Dual Temperature Response. *J. Am. Chem. Soc.* **140**, 13272–13284 (2018).

40. Hendriks, B., Waelkens, J., Winne, J. M. & Du Prez, F. E. Poly(thioether) Vitrimers via Transalkylation of Trialkylsulfonium Salts. *ACS Macro Lett.* **6**, 930–934 (2017).

41. Li, Y., Liu, T., Zhang, S., Shao, L., Fei, M., Yu, H., & Zhang, J. Catalyst-free vitrimer elastomers based on a dimer acid: robust mechanical performance, adaptability and hydrothermal recyclability. *Green Chem.* **22**, 870–881 (2020).

42. Wang, S., Teng, N., Dai, J., Liu, J., Cao, L., Zhao, W. & Liu, X. Taking Advantages of Intramolecular Hydrogen Bonding to Prepare Mechanically Robust and Catalyst-free Vitrimer. *Polymer* **210**, 123004 (2020).

43. Guerre, M., Taplan, C., Winne, J. M. & Du Prez, F. E. Vitrimers: directing chemical reactivity to control material properties. *Chemical Science* **11**, 4855–4870 (2020).

44. Cromwell, O. R., Chung, J. & Guan, Z. Malleable and Self-Healing Covalent Polymer Networks through Tunable Dynamic Boronic Ester Bonds. *J. Am. Chem. Soc.* **137**, 6492–6495 (2015).

45. 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.* **139**, 14881–14884 (2017).

46. Van Lijsebetten, F., Holloway, J. O., Winne, J. M. & Du Prez, F. E. Internal catalysis for dynamic covalent chemistry applications and polymer science. *Chem. Soc. Rev*. (2020). doi:10.1039/d0cs00452a

47. 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.* **141**, 15277−15287 (2019).

48. Zhang, H., Majumdar, S., Van Benthem, R. A. T. M., Sijbesma, R. P. & Heuts, J. P. A. Intramolecularly Catalyzed Dynamic Polyester Networks Using Neighboring Carboxylic and Sulfonic Acid Groups. *ACS Macro Lett.* **9**, 272–277 (2020).

49. Ramjit, H. G. & Sedgwick, R. D. The Kinetics of Ester-Ester Exchange Reactions by Mass Spectrometry. *J. Macromol. Sci. Part A - Chem.* **10**, 815–824 (1976).

50. Talapatra, K. Studies in ester interchange reactions in glycerides. Doctoral dissertation, University of Calcutta, 1968

51. Otera, J. Transesterification. *Chem. Rev* **93**, 1449-1470 (1993).

52. Kursanov, D. N., Korshak, V. V. & Vinogradova, S. V. Investigation of the polyester exchange reaction by the use of deuterium. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **2**, 125–128 (1953).

53. Kotliar, A. M. Interchange reactions involving condensation polymers. *J. Polym. Sci. Macromol. Rev.* **16**, 367–395 (1981).

54. Riemenschneider, W. & Bolt, H. M. Esters, Organic. in *Ullmann's Encyclopedia of Industrial Chemistry*; Ed.; Wiley-VCH Verlag GmbH & Co. KGaA, 2005, pp. 645-266

55. McCullagh, C. M. & Blackwell, J. 10 - Structure and Properties of Aromatic Liquid Crystalline Copolyesters. in *Comprehensive Polymer Science and Supplements; Allen, G., Bevington, J. C., Eds.;* Pergamon, 1989, pp. 389–410

56. Medina, R. M., Likhatchev, D., Alexandrova, L., Sánchez-Solís, A. & Manero, O. Mechanism and kinetics of transesterification in poly(ethylene terephthalate) and poly(ethylene 2,6-naphthalene dicarboxylate) polymer blends. *Polymer* **45**, 8517–8522 (2004).

57. Parker, V. D. & Baker, A. W. The Mechanism of Ester Acidolysis. *Chem. Commun. (London)* (1968).

58. Li, T., Zhang, X., Zhang, C., Li, R., Liu, J., Zhang, H. A Density Functional Theory Study on the Acid-Catalyzed Transesterification Mechanism for Biodiesel Production from Waste Cooking Oils. *J. Am. Oil Chem. Soc.* **96**, 137-145 (2019).

59. Li, X. Y., Jiang, J. C., Wang, K., Li, K. & Gao, Y. W. Reaction Mechanism and Impact Factors Analysis of Transesterification Biodiesel Production. *Adv. Mater. Res.* **343–344**, 222–226 (2011).

60. Goodman, I. & Nesbitt, B. F. The structures and reversible polymerization of cyclic oligomers from poly(ethylene terephthalate). *Polymer.* **1**, 384–396 (1960).

61. Lai, C.-L., Lee, H. M. & Hu, C.-H. Theoretical study on the mechanism of N-heterocyclic carbene catalyzed transesterification reactions. *Tetrahedron Lett.* **46**, 6265–6270 (2005).

62. Liu, X., He, H., Wang, Y., Zhu, S. & Piao, X. Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst. *Fuel* **87**, 216–221 (2008).

63. Guo, F., Wei, N.-N., Xiu, Z.-L. & Fang, Z. Transesterification mechanism of soybean oil to biodiesel catalyzed by calcined sodium silicate. *Fuel* **93**, 468–472 (2012).

64. Lin, L., Silva Gomes, E., Payan, F., Jaber, M., Krafft, J-M., Laugel, G., Lauron-Pernot, H. How the acido-basic properties of Mg silicates and clays govern the catalytic mechanism of transesterification reactions. *Catal. Sci. Technol.* **9**, 6072–6084 (2019).

65. Guan, Q., Shang, H., Liu, J., Gu, J., Li, B., Miao, R., Chen, Q., Ning, P. Biodiesel from transesterification at low temperature by AlCl3 catalysis in ethanol and carbon dioxide as cosolvent: Process, mechanism and application. *Appl. Energy* **164**, 380–386 (2016).

66. Santacesaria, E., Trulli, F., Minervini, L., Di Serio, M.,Tesser, R., Contessa, S. Kinetic and catalytic aspects in melt transesterification of dimethyl terephthalate with ethylene glycol. *J. Appl. Polym. Sci.* **54**, 1371–1384 (1994).

67. Hsu, J.-P. & Wong, J.-J. Kinetic modeling of melt transesterification of diphenyl carbonate and bisphenol-A. *Polymer* **44**, 5851–5857 (2003).

68. Harris, R. F. & Lopez, K. M. Reactions of glycerol with poly(ethylene ether carbonate) polyols. *J. Appl. Polym. Sci.* **44**, 1663–1670 (1992).

69. Bi, F.-L., Xi, Z.-H. & Zhao, L. Reaction Mechanisms and Kinetics of the Melt Transesterification of Bisphenol-A and Diphenyl Carbonate. *Int. J. Chem. Kinet.* **50**, 188–203 (2018).

70. Fan, M. & Zhang, P. Activated Carbon Supported K_2CO_3 Catalysts for Transesterification of Dimethyl Carbonate with Propyl Alcohol. *Energy & Fuels* **21**, 633–635 (2007).

71. Shaikh, A. A. G. & Sivaram, S. Dialkyl and diaryl carbonates by carbonate interchange reaction with dimethyl carbonate. *Ind. Eng. Chem. Res.* **31**, 1167–1170 (1992).

72. Du, Z., Xiao, Y., Chen, T. & Wang, G. Catalytic study on the transesterification of dimethyl carbonate and phenol to diphenyl carbonate. *Catal. Commun.* **9**, 239–243 (2008).

73. Liang, Y., Su, K., Cao, L., Gao, Y. & Li, Z. Study on the transesterification and mechanism of bisphenol A and dimethyl carbonate catalyzed by organotin oxide. *Chem. Pap.* **73**, 2171–2182 (2019).

74. Samuilov, A. Y. & Samuilov, Y. D. Theoretical study of transesterification of diethyl carbonate with methanol catalyzed by base and Lewis acid. *Theor. Chem. Acc.* **138**, 24 (2019).

75. Song, Z., Subramaniam, B. & Chaudhari, R. V. Kinetic modeling and mechanistic investigations of transesterification of propylene carbonate with methanol over an Fe–Mn double metal cyanide catalyst. *React. Chem. Eng.* **5**, 101–111 (2020).

76. Wang, Q., Li, C., Guo, M., Luo, S. & Hu, C. Transesterification of dimethyl carbonate with phenol to diphenyl carbonate over hexagonal $Mg(OH)_2$ nanoflakes. *Inorg. Chem. Front.* **2**, 47–54 (2015).

77. Song, Z., Jin, X., Hu, Y., Subramaniam, B. & Chaudhari, R. V. Intriguing Catalyst (CaO) Pretreatment Effects and Mechanistic Insights during Propylene Carbonate Transesterification with Methanol. *ACS Sustain. Chem. Eng.* **5**, 4718–4729 (2017).

78. Song, Z., Subramaniam, B. & Chaudhari, R. V. Kinetic Study of CaO-Catalyzed Transesterification of Cyclic Carbonates with Methanol. *Ind. Eng. Chem. Res.* **57**, 14977–14987 (2018).

79. Samuilov, A. Y., Korshunov, M. V. & Samuilov, Y. D. Transesterification of Diethyl Carbonate with Methanol Catalyzed by Sodium Methoxide. *Russ. J. Org. Chem.* **55**, 1338–1343 (2019).

80. Crocellà, V., Tabanelli, T., Vitillo, J. G., Costenaro, D., Bisio, C., Cavani, F., Bordiga, S. A multi-technique approach to disclose the reaction mechanism of dimethyl carbonate synthesis over amino-modified SBA-15 catalysts. *Appl. Catal. B Environ.* **211**, 323–336

(2017).

81. Godard, P., Dekoninck, J. M., Devlesaver, V. & Devaux, J. Molten bisphenol-A polycarbonate—poly(ethylene terephthalate) blends. II. Kinetics of the exchange reaction. *J. Polym. Sci. Part A Polym. Chem.* **24**, 3315–3324 (1986).

82. Roettger, M. Associative exchange reactions of boron or nitrogen containing bonds and design of vitrimers. Doctoral dissertation, Université Pierre et Marie Curie, Paris VI, 2016.

83. Fujita, N., Shinkai, S. & James, T. D. Boronic Acids in Molecular Self-Assembly. *Chem. – An Asian J.* **3**, 1076–1091 (2008).

84. Marco-Dufort, B. & Tibbitt, M. W. Design of moldable hydrogels for biomedical applications using dynamic covalent boronic esters. *Mater. Today Chem.* **12**, 16–33 (2019).

85. Hall, D. G. Structure, Properties, and Preparation of Boronic Acid Derivatives. Overview of Their Reactions and Applications. in *Boronic Acids*; Hall, D. G., Ed.; Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, FRG, 2005; pp. 1–99

86. Mancini, R. S., Lee, J. B. & Taylor, M. S. Boronic esters as protective groups in carbohydrate chemistry: processes for acylation, silylation and alkylation of glycoside-derived boronates. *Org. Biomol. Chem.* **15**, 132–143 (2017).

87. Roy, D. & Sumerlin, B. S. Glucose-Sensitivity of Boronic Acid Block Copolymers at Physiological pH. *ACS Macro Lett.* **1**, 529–532 (2012).

88. Wang, L., Zhang, J., Kim, B.,Peng, J., Berry, S. N., Ni, Y., Su, D., Lee, J., Yuan, L., Chang, Y-T. Boronic Acid: A Bio-Inspired Strategy To Increase the Sensitivity and Selectivity of Fluorescent NADH Probe. *J. Am. Chem. Soc.* **138**, 10394–10397 (2016).

89. Liu, J., Yang, K., Shao, W., Qu, Y., Li, S., Wu, Q., Zhang, L., Zhang, Y. Boronic Acid-Functionalized Particles with Flexible Three-Dimensional Polymer Branch for Highly Specific Recognition of Glycoproteins. *ACS Appl. Mater. Interfaces* **8**, 9552–9556 (2016).

90. Brooks, W. L. A. & Sumerlin, B. S. Synthesis and Applications of Boronic Acid-Containing Polymers: From Materials to Medicine. *Chem. Rev.* **116**, 1375–1397 (2016).

91. Zhao, Z., Yao, X., Zhang, Z., Chen, L., He, C., Chen, X. Boronic Acid Shell-Crosslinked Dextran- b- PLA Micelles for Acid-Responsive Drug Delivery. *Macromol. Biosci.* **14**, 1609–1618 (2014).

92. Yang, H., Zhang, C., Li, C., Liu, Y., An, Y., Ma, R., Shi, L. Glucose-Responsive Polymer Vesicles Templated by α-CD/PEG Inclusion Complex. *Biomacromolecules* **16**, 1372–1381 (2015).

93. Crane, B. C., Barwell, N. P., Gopal, P., Gopichand, M., Higgs, T., James, T. D., Jones, C. M., Mackenzie, A., Mulavisala, K. P., Paterson, W. The Development of a Continuous Intravascular Glucose Monitoring Sensor. *J. Diabetes Sci. Technol.* **9**, 751–761 (2015).

94. Sun, X. & James, T. D. Glucose Sensing in Supramolecular Chemistry. *Chem. Rev.* **115**, 8001–8037 (2015).

95. Bernardini, R., Oliva, A., Paganelli, A., Menta, E., Grugni, M., De Munari, S., Goldoni, L. Stability of Boronic Esters to Hydrolysis: A Comparative Study. *Chem. Lett.* **38**, 750–751 (2009).

96. Li, H., Li, H., Dai, Q., Li, H. & Brédas, J.-L. Hydrolytic Stability of Boronate Ester-Linked Covalent Organic Frameworks. *Adv. Theory Simulations* **1**, 1700015 (2018).

97. Deng, C. C., Brooks, W. L. A., Abboud, K. A. & Sumerlin, B. S. Boronic Acid-Based Hydrogels Undergo Self-Healing at Neutral and Acidic pH. *ACS Macro Lett.* **4**, 220–224 (2015).

98. Dong, Y., Wang, W., Veiseh, O., Appel, E. A., Xue, K., Webber, M. J., Tang, B. C., Yang, X-W., Weir, G. C., Langer, R., Anderson, D. G.Injectable and Glucose-Responsive Hydrogels Based on Boronic Acid–Glucose Complexation. *Langmuir* **32**, 8743–8747 (2016).

99. Pettignano, A., Grijalvo, S., Häring, M., Eritja, R., Tanchoux, N., Quignard, F., Díaz Díaz, D. Boronic acid-modified alginate enables direct formation of injectable, self-healing and multistimuli-responsive hydrogels. *Chem. Commun.* **53**, 3350–3353 (2017).

100. Cash, J. J., Kubo, T., Bapat, A. P. & Sumerlin, B. S. Room-Temperature Self-Healing Polymers Based on Dynamic-Covalent Boronic Esters. *Macromolecules* **48**, 2098–2106 (2015).

101. Cash, J. J., Kubo, T., Dobbins, D. J. & Sumerlin, B. S. Maximizing the symbiosis of static and dynamic bonds in self-healing boronic ester networks. *Polym. Chem.* **9**, 2011–2020 (2018).

102. Kasemsiri, P., Lorwanishpaisarn, N., Pongsa, U. & Ando, S. Reconfigurable Shape Memory and Self-Welding Properties of Epoxy Phenolic Novolac/Cashew Nut Shell Liquid Composites Reinforced with Carbon Nanotubes. *Polymers* **10**, 482 (2018).

103. Röttger, M., Domenech, T., Van Der Weegen, R., Breuillac, A., Nicolaÿ, R., Leibler, L. High-performance vitrimers from commodity thermoplastics through dioxaborolane metathesis. *Science (80-.).* **356**, 62–65 (2017).

104. Winne, J. M., Leibler, L. & Du Prez, F. E. Dynamic covalent chemistry in polymer networks: A mechanistic perspective. *Polymer Chemistry* **10**, 6091–6108 (2019).

105. Brunet, J., Collas, F., Humbert, M., Perrin, L., Brunel, F., Lacôte, E., Montarnal, D. & Raynaud, J. High Glass-Transition Temperature Polymer Networks Harnessing the Dynamic Ring Opening of Pinacol Boronates. *Angew. Chemie Int. Ed.* **58**, 12216–12222 (2019).

106. Nessler, C. US Patent 1,052,167, 1913.

107. Sastri, V. R. & Tesoro, G. C. Reversible crosslinking in epoxy resins. II. New approaches. *J. Appl. Polym. Sci.* **39**, 1439–1457 (1990).

108. Tesoro, G. C. & Sastri, V. Reversible crosslinking in epoxy resins. I. Feasibility studies. *J. Appl. Polym. Sci.* **39**, 1425–1437 (1990).

109. Stern, M. D. & Tobolsky, A. V. Stress-Time-Temperature Relations in Polysulfide Rubbers. *Rubber Chem. Technol.* **19**, 1178–1192 (1946).

110. Matxain, J. M., Asua, J. M. & Ruipérez, F. Design of new disulfide-based organic compounds for the improvement of self-healing materials. *Phys. Chem. Chem. Phys.* **18**, 1758–1770 (2016).

111. Azcune, I. & Odriozola, I. Aromatic disulfide crosslinks in polymer systems: Self-healing, reprocessability, recyclability and more. *Eur. Polym. J.* **84**, 147–160 (2016).

112. Martin, R., Rekondo, A., de Luzuriaga, A. R., Casuso, P., Dupin, D., Cabañero, G., Grande, H. J., Odriozola, I. Dynamic sulfur chemistry as a key tool in the design of self-healing polymers. *Smart Mater. Struct.* **25**, 084017 (2016).

113. Nevejans, S., Ballard, N., Miranda, J. I., Reck, B. & Asua, J. M. The underlying mechanisms for self-healing of poly(disulfide)s. *Phys. Chem. Chem. Phys.* **18**, 27577–27583 (2016).

114. Michal, B. T., Jaye, C. A., Spencer, E. J. & Rowan, S. J. Inherently photohealable and thermal shape-memory polydisulfide networks. *ACS Macro Lett.* **2**, 694–699 (2013).

115. Belenguer, A. M., Friščić, T., Day, G. M. & Sanders, J. K. M. Solid-state dynamic combinatorial chemistry: reversibility and thermodynamic product selection in covalent mechanosynthesis. *Chem. Sci.* **2**, 696 (2011).

116. Rekondo, A., Martin, R., Ruiz de Luzuriaga, A., Cabañero, G., Grande, H. J., Odriozola, I. Catalyst-free room-temperature self-healing elastomers based on aromatic disulfide metathesis. *Mater. Horiz.* **1**, 237–240 (2014).

117. Fernandes, P. A. & Ramos, M. J. Theoretical Insights into the Mechanism for Thiol/Disulfide Exchange. *Chem. - A Eur. J.* **10**, 257–266 (2004).

118. Bowman, C. N., Podgórski, M., Mavila, S., Huang, S., Spurgin, N., Sinha, J., Thiol-Anhydride Dynamic Reversible Networks. *Angew. Chemie Int. Ed.* **59**, 9345 (2020).

119. El-Zaatari, B. M., Ishibashi, J. S. A. & Kalow, J. A. Cross-linker control of vitrimer flow. *Polym. Chem.* **8**, 1–3 (2020).

120. Simonds, R. P. & Goethals, E. J. Cationic degradation of poly(propylene sulfide). *Die Makromol. Chemie* **179**, 1689–1697 (1978).

121. Simonds, R. P., Goethals, E. J. & Spassky, N. Cationic degradation of poly(propylene sulfide). Confirmation of the transalkylation reaction. *Die Makromol. Chemie* **179**, 1851–1853 (1978).

122. Vancraeynest, W. M. & Goethals, E. J. The formation of cyclic oligomers by cationic degradation of poly(phenylthiirane). *Die Makromol. Chemie* **179**, 2613–2619 (1978).

123. Liu, T., Qiu, R., Zhu, L., Yin, S-F., Au, C-T., Kambe, N. Alkyl Sulfides as Promising Sulfur Sources: Metal-Free Synthesis of Aryl Alkyl Sulfides and Dialkyl Sulfides by Transalkylation of Simple Sulfides with Alkyl Halides. *Chem. - An Asian J.* **13**, 3833–3837 (2018).

124. Tang, Z., Liu, Y., Huang, Q., Zhao, J., Guo, B., Zhang, L. A real recycling loop of sulfur-cured rubber through transalkylation exchange of C–S bonds. *Green Chem.* **20**, 5454–5458 (2018).

125. Corden, C., Tyrer, D., Menadue, H., Calero, J., Dade, J., Leferink, R. *Global Silicones Council Socio-economic evaluation of the global silicones industry Final Report*; Global Silicones Council; Amec Foster Wheeler Environment & Infrastructure UK Limited, 2016.

126. Osthoff, R. C., Bueche, A. M. & Grubb, W. T. Chemical Stress-Relaxation of Polydimethylsiloxane Elastomers *J. Am. Chem. Soc.* **76**, 4659–4663 (1954).

127. Kantor, S. W., Grubb, W. T. & Osthoff, R. C. The Mechanism of the Acid- and Base-catalyzed Equilibration of Siloxanes. *J. Am. Chem. Soc.* **76**, 5190–5197 (1954).

128. Buese, M. A. & Chang, P.-S. US Patent 5,347,028, 1994.

129. Zheng, P. & McCarthy, T. J. A Surprise from 1954: Siloxane Equilibration Is a Simple, Robust, and Obvious Polymer Self-Healing Mechanism. *J. Am. Chem. Soc.* **134**, 2024–2027 (2012).

130. Schmolke, W., Perner, N. & Seiffert, S. Dynamically Cross-Linked Polydimethylsiloxane Networks with Ambient-Temperature Self-Healing. *Macromolecules* **48**, 8781–8788 (2015).

131. Angot, F. Élastomères siloxanes à liens dynamiques. Doctoral dissertation, Université Pierre et Marie Curie, Paris VI, 2016.

132. Tretbar, C. A., Neal, J. A. & Guan, Z. Direct Silyl Ether Metathesis for Vitrimers with Exceptional Thermal Stability. *J. Am. Chem. Soc.* **141**, 16595–16599 (2019).

133. Geyer, R., Jambeck, J. R. & Law, K. L. Production, use, and fate of all plastics ever made. *Sci. Adv.* **3**, e1700782 (2017).

134. Offenbach, J. A. & Tobolsky, A. V. Chemical relaxation of stress in polyurethane elastomers. *J. Colloid Sci.* **11**, 39–47 (1956).

135. Colodny, P. C. & Tobolsky, A. V. Chemorheological Study of Polyurethan Elastomers *J. Am. Chem. Soc.* **79**, 4320–4323 (1957).

136. Jiang, L., Liu, Z., Lei, Y., Yuan, Y., Wu, B., Lei, J. Sustainable Thermosetting Polyurea Vitrimers Based on a Catalyst-Free Process with Reprocessability, Permanent Shape Reconfiguration and Self-Healing Performance. *ACS Appl. Polym. Mater.* **1**, 3261–3268 (2019).

137. Delebecq, E., Pascault, J.-P., Boutevin, B. & Ganachaud, F. On the Versatility of Urethane/Urea Bonds: Reversibility, Blocked Isocyanate, and Non-isocyanate Polyurethane. *Chem. Rev.* **113**, 80–118 (2013).

138. 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 Sustain. Chem. Eng.* **6**, 11145–11159 (2018).

139. Brutman, J. P., Fortman, D. J., De Hoe, G. X., Dichtel, W. R. & Hillmyer, M. A. Mechanistic Study of Stress Relaxation in Urethane-Containing Polymer Networks. *J. Phys. Chem. B* **123**, 1432–1441 (2019).

140. Deshpande, S. R., Likhite, A. P. & Rajappa, S. Transesterification of alkyl carbamate to aryl carbamate : Effect of varying the alkyl group. *Tetrahedron* **50**, 10367–10370 (1994).

141. Ying, H., Zhang, Y. & Cheng, J. Dynamic urea bond for the design of reversible and self-healing polymers. *Nat. Commun.* **5**, 3218 (2014).

142. Ying, H. & Cheng, J. Hydrolyzable Polyureas Bearing Hindered Urea Bonds. *J. Am. Chem. Soc.* **136**, 16974–16977 (2014).

143. Zhang, Y., Ying, H., Hart, K. R., Wu, Y., Hsu, A. J., Coppola, A. M., Kim, T. A., Yang, K., Sottos, N. R., White, S. R., Cheng, J. Malleable and Recyclable Poly(urea-urethane) Thermosets bearing Hindered Urea Bonds. *Adv. Mater.* **28**, 7646–7651 (2016).

144. Gamardella, F.; De la Flor, S.; Ramis, X.; Serra, A. Recyclable poly(thiourethane) vitrimers with high Tg. Influence of the isocyanate structure. Reactive and Functional Polymers 2020, 151, 104574."

145. Li, L., Chen, X. & Torkelson, J. M. Reprocessable Polymer Networks via Thiourethane Dynamic Chemistry: Recovery of Cross-link Density after Recycling and Proof-of-Principle Solvolysis Leading to Monomer Recovery. *Macromolecules* **52**, 8207–8216 (2019).

146. 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.* **137**, 14019–14022 (2015).

147. Fortman, D. J., Brutman, J. P., Hillmyer, M. A. & Dichtel, W. R. Structural effects on the reprocessability and stress relaxation of crosslinked polyhydroxyurethanes. *J. Appl. Polym. Sci.* **134**, 44984 (2017).

148. Chen, X., Li, L., Jin, K. & Torkelson, J. M. Reprocessable polyhydroxyurethane networks exhibiting full property recovery and concurrent associative and dissociative dynamic chemistry via transcarbamoylation and reversible cyclic carbonate aminolysis. *Polym. Chem.* **8**, 6349-6355 (2017).

149. Schneider, V. & Frolich, P. K. Mechanism of Formation of Aromatics from Lower Paraffins 1,2. *Ind. Eng. Chem.* **23**, 1405–1410 (1931).

150. *Olefin Metathesis Theory and Practice*; Grela K., Ed.; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2014

151. Calderon, N., Chen, H. Y. & Scott, K. W. Olefin metathesis - A novel reaction for skeletal transformations of unsaturated hydrocarbons. *Tetrahedron Lett.* **8**, 3327–3329 (1967).

152. *Handbook of Metathesis (3 Volume Set)*; Grubbs, R. H., Ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2003; Vol. **1**–**3**

153. Chauvin, Y. Olefin Metathesis: The Early Days (Nobel Lecture). *Angew. Chemie Int. Ed.* **45**, 3740–3747 (2006).

154. Schrock, R. R. Multiple Metal–Carbon Bonds for Catalytic Metathesis Reactions (Nobel Lecture). *Angew. Chemie Int. Ed.* **45**, 3748–3759 (2006).

155. Grubbs, R. H. Olefin-Metathesis Catalysts for the Preparation of Molecules and Materials (Nobel Lecture). *Angew. Chemie Int. Ed.* **45**, 3760–3765 (2006).

156. Jean-Louis Hérisson, P. & Chauvin, Y. Catalyse de transformation des oléfines par les complexes du tungstène. II. Télomérisation des oléfines cycliques en présence d'oléfines acycliques. *Die Makromol. Chemie* **141**, 161–176 (1971).

157. Grubbs, R. H. & Brunck, T. K. Possible intermediate in the tungsten-catalyzed olefin metathesis reaction. *J. Am. Chem. Soc.* **94**, 2538–2540 (1972).

158. Grubbs, R. H., Burk, P. L. & Carr, D. D. Mechanism of the olefin metathesis reaction. *J. Am. Chem. Soc.* **97**, 3265–3267 (1975).

159. Grubbs, R. H., Carr, D. D., Hoppin, C. & Burk, P. L. Consideration of the mechanism of the metal catalyzed olefin metathesis reaction. *J. Am. Chem. Soc.* **98**, 3478–3483 (1976).

160. Lu, Y.-X. X., Tournilhac, F., Leibler, L. & Guan, Z. Making insoluble polymer networks malleable via olefin metathesis. *J. Am. Chem. Soc.* **134**, 8424–8427 (2012).

161. Lu, Y.-X. & Guan, Z. Olefin Metathesis for Effective Polymer Healing via Dynamic Exchange of Strong Carbon–Carbon Double Bonds. *J. Am. Chem. Soc.* **134**, 14226–14231 (2012).

162. Cerqueira, N. M. F. S. A., Fernandes, P. A. & Ramos, M. J. Computational Mechanistic Studies Addressed to the Transimination Reaction Present in All Pyridoxal 5'-Phosphate-Requiring Enzymes. *J. Chem. Theory Comput.* **7**, 1356–1368 (2011).

163. 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.* **26**, 3938–3942 (2014).

164. 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.* **55**, 2011–2018 (2017).

165. Liu, H., Zhang, H., Wang, H., Huang, X., Huang, G., Wu, J. Weldable, malleable and programmable epoxy vitrimers with high mechanical properties and water insensitivity. *Chem. Eng. J.* **368**, 61–70 (2019).

166. Hajj, R., Duval, A., Dhers, S. & Avérous, L. Network Design to Control Polyimine Vitrimer Properties: Physical Versus Chemical Approach. *Macromolecules* **53**, 3796–3805 (2020).

167. Snyder, R. L., Lidston, C. A. L., De Hoe, G. X., Parvulescu, M. J. S., Hillmyer, M. A., Coates, G. W. Mechanically robust and reprocessable imine exchange networks from modular polyester pre-polymers. *Polym. Chem.* **11**, 5346-5355 (2020).

168. Wang, S., Ma, S., Li, Q., Yuan, W., Wang, B., Zhu, J. Robust, Fire-Safe, Monomer-Recovery, Highly Malleable Thermosets from Renewable Bioresources. *Macromolecules* **51**, 8001–8012 (2018).

169. Zhao, S. & Abu-Omar, M. M. Recyclable and Malleable Epoxy Thermoset Bearing Aromatic Imine Bonds. *Macromolecules* **51**, 9816–9824 (2018).

170. Geng, H., Wang, Y., Yu, Q., Gu, S., Zhou, Y., Xu, W., Zhang, X., Ye, D. Vanillin-Based Polyschiff Vitrimers: Reprocessability and Chemical Recyclability. *ACS Sustain. Chem. Eng.* **6**, 15463–15470 (2018).

171. Liu, Y., Tang, Z., Chen, Y., Wu, S. & Guo, B. Programming dynamic imine bond into elastomer/graphene composite toward mechanically strong, malleable, and multi-stimuli responsive vitrimer. *Compos. Sci. Technol.* **168**, 214–223 (2018).

172. Zheng, H., Liu, Q., Lei, X., Chen, Y., Zhang, B., Zhang, Q. A conjugation polyimine vitrimer: Fabrication and performance. *J. Polym. Sci. Part A Polym. Chem.* **56**, 2531–2538 (2018).

173. Dhers, S., Vantomme, G. & Avérous, L. A fully bio-based polyimine vitrimer derived from fructose. *Green Chem.* **21**, 1596–1601 (2019).

174. Feng, Z., Yu, B., Hu, J., Zuo, H., Li, J., Sun, H., Ning, N., Tian, M., Zhang, L. Multifunctional Vitrimer-Like Polydimethylsiloxane (PDMS): Recyclable, Self-Healable, and Water-Driven Malleable Covalent Networks Based on Dynamic Imine Bond. *Ind. Eng. Chem. Res.* **58**, 1212–1221 (2019).

175. Yu, Q., Peng, X., Wang, Y., Geng, H., Xu, A., Zhang, X., Xu, W., Ye, D. Vanillin-based degradable epoxy vitrimers: Reprocessability and mechanical properties study. *Eur. Polym. J.* **117**, 55–63 (2019).

176. Hogg, J. L., Jencks, D. A. & Jencks, W. P. Catalysis of transimination through trapping by acids and bases. *J. Am. Chem. Soc.* **99**, 4772–4778 (1977).

177. Boate, A. R. & Eaton, D. R. Metal complex catalyzed reactions of anils. II. Transimination. *Can. J. Chem.* **55**, 2426–2431 (1977).

178. Salvà, A., Donoso, J., Frau, J. & Muñoz, F. Density Functional Theory Studies on Transimination of Vitamin B6 Analogues through Geminal Diamine Formation. *J. Phys. Chem. A* **108**, 11709–11714 (2004).

179. Ciaccia, M., Cacciapaglia, R., Mencarelli, P., Mandolini, L. & Di Stefano, S. Fast transimination in organic solvents in the absence of proton and metal catalysts. A key to imine metathesis catalyzed by primary amines under mild conditions. *Chem. Sci.* **4**, 2253 (2013).

180. Ciaccia, M., Pilati, S., Cacciapaglia, R., Mandolini, L. & Di Stefano, S. Effective catalysis of imine metathesis by means of fast transiminations between aromatic–aromatic or aromatic–aliphatic amines. *Org. Biomol. Chem.* **12**, 3282–3287 (2014).

181. Ciaccia, M. & Di Stefano, S. Mechanisms of imine exchange reactions in organic solvents. *Org. Biomol. Chem.* **13**, 646–654 (2015).

182. Tóth, G., Pintér, I. & Messmer, A. Mechanism of the exchange reaction of aromatic Schiff bases. *Tetrahedron Lett.* **15**, 735–738 (1974).

183. Abdulla, R. F., Emmick, T. L. & Taylor, H. M. A New Synthetic Approach to 4(1H)-Pyridone Derivatives. I. 1-Alkyl-3,5-diaryl-4(1H)-pyridones. *Synth. Commun.* **7**, 305–312 (1977).

184. Friary, R. J., Seidl, V., Schwerdt, J. H., Chan, T-M., Cohen, M. P., Conklin, E. R., Duelfer, T., Hou, D., Nafissi, M., Runkle, R. L., Tahbaz, P., Tiberi, R. L., Mc Phail, A. T. Intermolecular transaminations of enaminones: a synthesis of fused, polycyclic, N-aryl pyridones. *Tetrahedron* **49**, 7179–7192 (1993).

185. Ostrowska, K., Ciechanowicz-Rutkowska, M., Pilati, T. & Zżuchowski, G. Synthesis and Transamination of Enaminones: Derivatives of 1-Phenyl-4-(phenylhydroxymethylidene)-pyrrolidine-2,3,5-trione. *Monatshefte für Chemie / Chem. Mon.* **130**, 555–562 (1999).

186. Sanchez-Sanchez, A., Fulton, D. A. & Pomposo, J. A. pH-responsive single-chain polymer nanoparticles utilising dynamic covalent enamine bonds. *Chem. Commun.* **50**, 1871–1874 (2014).

187. 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.* **8**, 14857 (2017).

188. Bai, L. & Zheng, J. Robust, reprocessable and shape-memory vinylogous urethane vitrimer composites enhanced by sacrificial and self-catalysis Zn(II)–ligand bonds. *Compos. Sci. Technol.* **190**, 108062 (2020).

189.

190. Spiesschaert, Y., Taplan, C., Stricker, L., Guerre, M., Winne, J. M., Du Prez, F. E. Influence of the polymer matrix on the viscoelastic behaviour of vitrimers. *Polym. Chem.* **11**, 5377-5385 (2020).

191. Haida, P. & Abetz, V. Acid-Mediated Autocatalysis in Vinylogous Urethane Vitrimers. *Macromol. Rapid Commun.* **41**, 2000273 (2020).

192. Spiesschaert, Y., Guerre, M., Imbernon, L., Winne, J. M. & Du Prez, F. Filler reinforced polydimethylsiloxane-based vitrimers. *Polymer* **172**, 239–246 (2019).

193. Liu, H., Sui, X., Xu, H., Zhang, L., Zhong, Y., Mao, Z. Self-Healing Polysaccharide Hydrogel Based on Dynamic Covalent Enamine Bonds. *Macromol. Mater. Eng.* **301**, 725–732 (2016).

194. Zhang, Y., Yuan, L., Guan, Q., Liang, G. & Gu, A. Developing self-healable and antibacterial polyacrylate coatings with high mechanical strength through crosslinking by multi-amine hyperbranched polysiloxane via dynamic vinylogous urethane. *J. Mater. Chem. A* **5**, 16889–16897 (2017).

195. Stukenbroeker, T., Wang, W., Winne, J. M., Du Prez, F. E., Nicolaÿ, R., Leibler, L. Polydimethylsiloxane quenchable vitrimers. *Polym. Chem.* **8**, 6590–6593 (2017).

196. Liu, Z., Zhang, C., Shi, Z., Yin, J. & Tian, M. Tailoring vinylogous urethane chemistry for the cross-linked polybutadiene: Wide freedom design, multiple recycling methods, good shape memory behavior. *Polymer* **148**, 202–210 (2018).

197. 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* **52**, 2105–2111 (2019).

198. Lessard, J. J., Scheutz, G. M., Hughes, R. W. & Sumerlin, B. S. Polystyrene-Based Vitrimers: Inexpensive and Recyclable Thermosets. *ACS Appl. Polym. Mater.* **2**, 8, 3044–3048 (2020).

199. Spiesschaert, Y., Guerre, M., De Baere, I., Van Paepegem, W., Winne, J. M., Du Prez, F. E. Dynamic Curing Agents for Amine-Hardened Epoxy Vitrimers with Short (Re)processing Times. *Macromolecules* **53**, 2485–2495 (2020).

200. Wright, T., Tomkovic, T., Hatzikiriakos, S. G. & Wolf, M. O. Photoactivated Healable Vitrimeric Copolymers. *Macromolecules* **52**, 36–42 (2019).

201. Augustyns, K., Kraas, W. & Jung, G. Investigation on the stability of the Dde protecting group used in peptide synthesis: migration to an unprotected lysine1. *J. Pept. Res.* **51**, 127–133 (1998).

202. Rohwedder, B., Mutti, Y., Dumy, P. & Mutter, M. Hydrazinolysis of Dde: Complete orthogonality with Aloc protecting groups. *Tetrahedron Lett.* **39**, 1175–1178 (1998).

203. Kocienski, P. J *Protecting Groups*; Georg Thieme Verlag: Stuttgart, 2005.

204. 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.* **11**, 442–448 (2019).

205. He, C., Christensen, P. R., Seguin, T. J., Dailing, E. A., Wood, B. M., Walde, R. K., Persson, K. A., Russell, T. P., Helms, B. A. Conformational Entropy as a Means to Control the Behavior of Poly(diketoenamine) Vitrimers In and Out of Equilibrium. *Angew. Chemie Int. Ed.* **59**, 735–739 (2020).

206. Boucher, D., Madsen, J., Caussé, N., Pébère, N., Ladmiral, V., Negrell, C. Hemiacetal Ester Exchanges, Study of Reaction Conditions and Mechanistic Pathway. *Reactions* **1**, 89–101 (2020).

207. Fife, T. H. & Benjamin, B. M. General base catalyzed intramolecular transesterification. *J. Am. Chem. Soc.* **95**, 2059–2061 (1973).

208. Wojtas, K. P., Lu, J.-Y., Krahn, D. & Arndt, H.-D. Regioselective Functionalization of 3-Hydroxy-pyridine Carboxylates by Neighboring Group Assistance. *Chem. - An Asian J.* **11**, 2859–2862 (2016).

209. Krivec, M., Perdih, F., Košmrlj, J. & Kočevar, M. Regioselective Hydrolysis and Transesterification of Dimethyl 3-Benzamidophthalates Assisted by a Neighboring Amide Group. *J. Org. Chem.* **81**, 5732–5739 (2016).

210. Nakanishi, W., Nakanishi, H., Yanagawa, Y., Ikeda, Y. & Oki, M. The effets of the neigboring methoxycarbonyl group and sulfur atom(s) in the carbon-sulfue bond cleavage and the ester exchange in fluorene systems. *Chem. Lett.* **12**, 105–108 (1983).

211. Bader, A. R. & Vogel, H. A. Transesterification. II. Esters of Strong Organic Acids. *J. Am. Chem. Soc* **74**, 3992–3994 (1952).

212. Debnath, S., Kaushal, S. & Ojha, U. Catalyst Free Partially Bio-Based Polyester Vitrimers. *ACS Appl. Polym. Mater.* **2, 2**, 1006–1013 (2020).

213. Shafer, J. A. & Morawetz, H. Hydrolysis of an Ester with a Neighboring Carboxyl and a Quaternary Ammonium Group. *J. Org. Chem.* **27**, 2269–2270 (1962).

214. Delahaye, M., Tanini, F., Holloway, J. O., Winne, J. M. & Du Prez, F. E. Double neighbouring group participation for ultrafast exchange in phthalate monoester networks. *Polym. Chem.* **11**, 5207-5215 (2020).

215. 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 the carboxylic acid/epoxy ratio based on facilely synthesized trifunctional monoesterified cyclic anhydrides. *Eur. Polym. J.* **135**, 109881 (2020).

216. Hao, C., Liu, T., Zhang, S., Liu, W., Shan, Y., Zhang, J. Triethanolamine-Mediated Covalent Adaptable Epoxy Network: Excellent Mechanical Properties, Fast Repairing, and Easy Recycling. *Macromolecules* **53**, 3110−3118 (2020). doi:10.1021/acs.macromol.9b02243

217. Li, Y., Liu, T., Zhang, S., Shao, L., Fei, M., Yu, H., Zhang, J. Catalyst-free vitrimer elastomers based on a dimer acid: robust mechanical performance, adaptability and hydrothermal recyclability. *Green Chem.* **22**, 870–881 (2020).

218. Altuna, F. I., Casado, U., Dell'Erba, I. E., Luna, L., Hoppe, C. E., Williams, R. J. J. Epoxy vitrimers incorporating physical crosslinks produced by self-association of alkyl chains. *Polym. Chem.* **11**, 1337–1347 (2020).

219. Giebler, M., Sperling, C., Kaiser, S., Duretek, I. & Schlögl, S. Epoxy-Anhydride Vitrimers from Aminoglycidyl Resins with High Glass Transition Temperature and Efficient Stress Relaxation. *Polymers* **12**, 1148 (2020).

220. Craun, G. P., Sobek, S. M. & Berghoff, W. F. US Patent 4,897,450, 1990.

221. Wang, S., Teng, N., Dai, J., Liu, J., Cao, L., Zhao, W., Liu, X. Taking Advantages of Intramolecular Hydrogen Bonding to Prepare Mechanically Robust and Catalyst-free Vitrimer. *Polymer* **210**, 123004 (2020).

222. Mu, S., Zhang, Y., Zhou, J., Wang, B. & Wang, Z. Recyclable and Mechanically Robust Palm Oil-Derived Epoxy Resins with Reconfigurable Shape-Memory Properties. *ACS Sustain. Chem. Eng.* **8**, 5296–5304 (2020).

223. 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.* **141**, 13753–13757 (2019).

224. Tillett, J. G. & Wiggins, D. E. Neighbouring hydroxyl group catalysis in the hydrolysis of carbonate esters. *Tetrahedron Lett.* **12**, 911–914 (1971).

225. Shaikh, A.-A. G. & Sivaram, S. Organic Carbonates. *Chem. Rev.* **96**, 951–976 (1996).

226. Brunelle, D. J. Transesterification Chemistry, Low Temperature Reactions of O-Nithophenyl Carbonates. *J. Macromol. Sci. Part A - Chem.* **28**, 95–102 (1991).

227. Kamps, J. H., Hoeks, T., Kung, E., Lens, J. P., McCloskey, P. J., Noordover, B. A. J., Heuts, J. P. A Activated carbonates: enabling the synthesis of differentiated polycarbonate resins via melt transcarbonation. *Polym. Chem.* **7**, 5294–5303 (2016).

228. Brunelle, D. J. & Smith, W. E. US Patent 4,349,486, 1982.

229. Sugiyama, M., Akiyama, M., Nishiyama, K., Okazoe, T. & Nozaki, K. Synthesis of Fluorinated Dialkyl Carbonates from Carbon Dioxide as a Carbonyl Source. *ChemSusChem* **13**, 1775–1784 (2020).

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

231. Zhao, W., Feng, Z., Liang, Z., Lv, Y., Xiang, F., Xiong, C., Duan, C., Dai, L., Ni, Y. Vitrimer-Cellulose Paper Composites: A New Class of Strong, Smart, Green, and Sustainable Materials. *ACS Appl. Mater. Interfaces* **11**, 36090–36099 (2019).

232. Brooks, W. L. A., Deng, C. C. & Sumerlin, B. S. Structure–Reactivity Relationships in Boronic Acid–Diol Complexation. *ACS Omega* **3**, 17863–17870 (2018).

233. Piest, M., Zhang, X., Trinidad, J. & Engbersen, J. F. J. pH-responsive, dynamically restructuring hydrogels formed by reversible crosslinking of PVA with phenylboronic acid functionalised PPO–PEO–PPO spacers (Jeffamines®). *Soft Matter* **7**, 11111 (2011).

234. Lauer, M., Boehnke, H., Grotstollen, R., Salehnia, M. & Wulff, G. Chemistry of binding sites. IV. Unusual increase in reactivity of arylboronic acids through neighboring groups. *Chem. Informationsd.* **16**, 132–133 (1985).

235. Martínez-Aguirre, M. A., Villamil-Ramos, R., Guerrero-Alvarez, J. A. & Yatsimirsky, A. K. Substituent Effects and pH Profiles for Stability Constants of Arylboronic Acid Diol Esters. *J. Org. Chem.* **78**, 4674–4684 (2013).

236. Figueiredo, T., Ogawa, Y., Jing, J., Cosenza, V., Jeacomine, I., Olsson, J. D. M., Gerfaud, T., Boiteau, J-G., Harris, C., Auzély-Velty, R. Self-crosslinking smart hydrogels through direct complexation between benzoxaborole derivatives and diols from hyaluronic acid. *Polym. Chem.* **8**, 1–3 (2020).

237. Wulff, G., Lauer, M. & Böhnke, H. Rapid Proton Transfer as Cause of an Unusually Large Neighboring Group Effect. *Angew.*

Chemie Int. Ed. English **23**, 741–742 (1984).

238. Zhu, L., Shabbir, S. H., Gray, M., Lynch, V. M., Sorey, S., Anslyn, E. V. A Structural Investigation of the N−B Interaction in an o-(N,N-Dialkylaminomethyl)arylboronate System. *J. Am. Chem. Soc.* **128**, 1222–1232 (2006).

239. Collins, B. E., Metola, P. & Anslyn, E. V. On the rate of boronate ester formation in ortho-aminomethyl-functionalised phenyl boronic acids. *Supramol. Chem.* **25**, 79–86 (2013).

240. Aoyagi, M., Ushioda, M., Seio, K. & Sekine, M. A new 2',3'-cis diol protecting group required for the solid-phase synthesis of capped oligonucleotide derivatives. *Nucleic Acids Symp. Ser.* **3**, 149–150 (2003).

241. Zhang, X., Wang, S., Jiang, Z., Li, Y. & Jing, X. Boronic Ester Based Vitrimers with Enhanced Stability via Internal Boron−Nitrogen Coordination. *J. Am. Chem. Soc.* **142**, 52, 21852–21860 (2020).

242. Ohishi, T., Iki, Y., Imato, K., Higaki, Y., Takahara, A., Otsuka, H. Insertion Metathesis Depolymerization of Aromatic Disulfide-containing Dynamic Covalent Polymers under Weak Intensity Photoirradiation. *Chem. Lett.* **42**, 1346–1348 (2013).

243. Ruipérez, F., Galdeano, M., Gimenez, E. & Matxain, J. M. Sulfenamides as Building Blocks for Efficient Disulfide-Based Self-Healing Materials. A Quantum Chemical Study. *ChemistryOpen* **7**, 248–255 (2018).

244. Sarma, R. J., Otto, S. & Nitschke, J. R. Disulfides, Imines, and Metal Coordination within a Single System: Interplay between Three Dynamic Equilibria. *Chem. - A Eur. J.* **13**, 9542–9546 (2007).

245. Caraballo, R., Rahm, M., Vongvilai, P., Brinck, T. & Ramström, O. Phosphine-catalyzed disulfide metathesis. *Chem. Commun.* 6603 (2008).

246. Yu, H., Wang, Y., Yang, H., Peng, K. & Zhang, X. Injectable self-healing hydrogels formed via thiol/disulfide exchange of thiol functionalized F127 and dithiolane modified PEG. *J. Mater. Chem. B* **5**, 4121 (2017).

247. Li, Z-J., Zhong, J., Liu, M-C., Rong, J-C., Yang, K., Zhou, J-Y., Shen, L., Gao, F., He, H-F. Investigation on Self-healing Property of Epoxy Resins Based on Disulfide Dynamic Links. *Chinese J. Polym. Sci.* **38**, 932–940 (2020).

248. Amamoto, Y., Otsuka, H., Takahara, A. & Matyjaszewski, K. Self-Healing of Covalently Cross-Linked Polymers by Reshuffling Thiuram Disulfide Moieties in Air under Visible Light. *Adv. Mater.* **24**, 3975–3980 (2012).

249. Wright, P. & Semlyen, J. Equilibrium ring concentrations and the statistical conformations of polymer chains: Part 3. Substituent effects in polysiloxane systems. *Polymer* **11**, 462–471 (1970).

250. Saed, M. O. & Terentjev, E. M. Catalytic Control of Plastic Flow in Siloxane-Based Liquid Crystalline Elastomer Networks. *ACS Macro Lett.* **9**, 749–755 (2020).

251. Berkefeld, A., Guerra, C. F., Bertermann, R., Troegel, D., Daiß, J. O., Stohrer, J., Bickelhaupt, F. M., Tacke, R. Silicon α-Effect: A Systematic Experimental and Computational Study of the Hydrolysis of C α- and C γ-Functionalized Alkoxytriorganylsilanes of the Formula Type $ROSiMe_2(CH_2)_nX$ (R = Me, Et; n = 1, 3; X = Functional Group). *Organometallics* **33**, 2721–2737 (2014).

252. Zych, A., Pinalli, R., Soliman, M., Vachon, J. & Dalcanale, E. Polyethylene vitrimers via silyl ether exchange reaction. *Polymer* **199**, 122567 (2020).

253. Liu, W-X., Zhang, C., Zhang, H., Zhao, N., Yu, Z-X., Xu, J. Oxime-Based and Catalyst-Free Dynamic Covalent Polyurethanes. *J. Am. Chem. Soc.* **139**, 8678–8684 (2017).

254. Subrayan, R. P., Zhang, S., Jones, F. N., Swarup, V. & Yezrielev, A. I. Reactions of phenolic ester alcohol with aliphatic isocyanates-Transcarbamoylation of phenolic to aliphatic urethane: a ^{13}C-NMR study. *J. Appl. Polym. Sci.* **77**, 2212–2228 (2000).

255. Mukaiyama, T. & Iwanami, M. On the Thermal Dissociation of Organic Compounds. XI. The Effects of the Substituents on the Thermal Dissociation of Urethans in Amine Solvent. *J. Am. Chem. Soc.* **79**, 73–76 (1957).

256. Young, Y. H., Lin, H. M. & Lin, M. Y. Studies of Thermal Transesterification of Phenylurethane by High Pressure Liquid Chromatograph. *J. Chinese Chem. Soc.* **25**, 225–229 (1978).

257. Mormann, W., Frank, P., Schupp, T. & Seel, K. Reactions of N-acetylcysteine adducts of aromatic (di)isocyanates with functional groups of organic molecules: transcarbamoylation reactions in aqueous buffer and in an organic solvent. *EXCLI J.* **7**, 19–43 (2008).

258. Chen, X., Hu, S., Li, L. & Torkelson, J. M. Dynamic Covalent Polyurethane Networks with Excellent Property and Cross-Link Density Recovery after Recycling and Potential for Monomer Recovery. *ACS Appl. Polym. Mater.* **2**, 2093–2101 (2020).

259. Zhang, D., Chen, H., Dai, Q., Xiang, C., Li, Y., Xiong, X., Zhou, Y., Zhang, J. Stimuli-Mild, Robust, Commercializable Polyurethane-Urea Vitrimer Elastomer via N,N'-Diaryl Urea Crosslinking. *Macromol. Chem. Phys.* **221**, 1900564 (2020).

260. 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 crosslinking degree. *Polym. Chem.* **11**, 1348–1355 (2020).

261. Giuseppone, N., Schmitt, J.-L., Schwartz, E. & Lehn, J.-M. Scandium(III) Catalysis of Transimination Reactions. Independent and Constitutionally Coupled Reversible Processes. *J. Am. Chem. Soc.* **127**, 5528–5539 (2005).

262. Schaufelberger, F., Hu, L. & Ramström, O. trans -Symmetric Dynamic Covalent Systems: Connected Transamination and

Transimination Reactions. *Chem. - A Eur. J.* **21**, 9776–9783 (2015).

263. Wang, S., Ma, S., Li, Q., Xu, X., Wang, B., Huang, K., Liu, Y., Zhu, J. Facile Preparation of Polyimine Vitrimers with Enhanced Creep Resistance and Thermal and Mechanical Properties via Metal Coordination. *Macromolecules* **53**, 2919-2931 (2020)

264. Okuyama, T., Nagamatsu, H., Kitano, M. & Fueno, T. Nucleophilic catalysis of hydrolysis of a Schiff base by amines. Intramolecular catalysis of transimination. *J. Org. Chem.* **51**, 1516–1521 (1986).

265. Toullec, J. & Razafindralambo, R. Intramolecular base catalysis in N-benzylideneaniline transimination by (dimethylamino)alkylamines in methanol. *J. Org. Chem.* **52**, 1646–1647 (1987).

266. 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* **49**, 6277–6284 (2016).

267. Aljuhani, M. A., Barman, S., Abou-Hamad, E., Gurinov, A., Ould-Chikh, S., Guan, E., Jedidi, A., Cavallo, L., Gates, B. C., Pelletier, J. D. A., Basset, J-M. Imine Metathesis Catalyzed by a Silica-Supported Hafnium Imido Complex. *ACS Catal.* **8**, 9440–9446 (2018).

268. Schaufelberger, F., Seigel, K. & Ramström, O. Hydrogen-Bond Catalysis of Imine Exchange in Dynamic Covalent Systems. *Chem. Eur. J.* **26** (2020).

269. Feng, Z., Jia, S., Chen, H. & You, L. Modulation of imine chemistry with intramolecular hydrogen bonding: Effects from ortho-OH to NH. *Tetrahedron* **76**, 131128 (2020).

270. Nawrot, D., Kolenič, M., Kuneš, J., Kostelansky, F., Miletin, M., Novakova, V., Zimcik, P. Transalkylation of alkyl aryl sulfides with alkylating agents. *Tetrahedron* **74**, 594–599 (2018).

271. Obadia, M. M., Mudraboyina, B. P., Serghei, A., Montarnal, D. & Drockenmuller, E. Reprocessing and Recycling of Highly Cross-Linked Ion-Conducting Networks through Transalkylation Exchanges of C–N Bonds. *J. Am. Chem. Soc.* **137**, 6078–6083 (2015).

272. Chakma, P., Digby, Z. A., Shulman, M. D., Kuhn, L. R., Morley, C. N., Sparks, J. L., Konkolewicz, D. Anilinium Salts in Polymer Networks for Materials with Mechanical Stability and Mild Thermally Induced Dynamic Properties. *ACS Macro Lett*. **8**, 95–100 (2019).

273. Chakma, P., Morley, C. N., Sparks, J. L. & Konkolewicz, D. Exploring How Vitrimer-like Properties Can Be Achieved from Dissociative Exchange in Anilinium Salts. *Macromolecules* **53**, 1233–1244 (2020).

1