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1 Neighboring Group Participation and internal catalysis effects on exchangeable 2 covalent bonds: Application to the thriving field of vitrimers chemistry

3

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9

10 Abstract

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

24 (I) Introduction

25

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

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

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

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

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

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

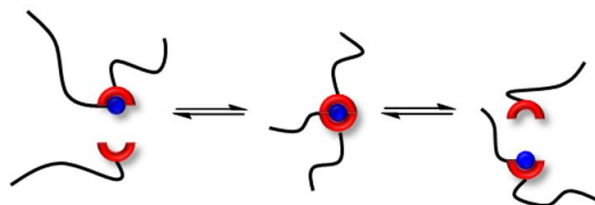
1 CANs somewhat blur the boundary with vitrimers.^{20,21,25,26} In addition, networks featuring both
2 permanent and exchangeable crosslinks are reported to exhibit vitrimer-like stress-relaxation, but
3 within a certain limit as the permanent crosslinks induced a residual stress plateau.²⁷ Such borderline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

6 Vitrimers address the problem of thermoset recyclability and thermoplastic vulnerability towards
7 solvents. Therefore, the interest for these materials is growing in industry, as highlighted in recent
8 reviews.^{22,28,29} Nonetheless some characteristics may limit their industrialization. They often display
9 high relaxation times and high viscosity during reprocessing, making them unsuitable for the
10 recycling processes usually found for thermoplastics in industry. Furthermore, most vitrimers rely on
11 catalysts and in some cases on high catalyst loadings.¹ The use of catalysts may generate problems
12 such as limited number of recycling/reshaping cycles due to premature degradation, or migration
13 and loss of the catalyst.³⁰⁻³² A solution to this issue is the design of vitrimers that do not rely on
14 catalysis. This can be done by using a large excess of exchanging functional groups³²⁻³⁴ or by using
15 exchange reactions which do not require any catalyst.^{18,35-42} Another strategy, inspired by organic
16 chemistry in solutions, relies on chemical functions near the exchangeable bond to enhance the
17 reaction rate. This effect is called either neighboring group participation (NGP) when the accelerating
18 substituents are at some point covalently bonded to the reaction center during the exchange, or
19 internal catalysis for effects at longer distance such as electrostatic interactions, steric effects or
20 weak bonds.⁴³ Guan et al.⁴⁴ implemented this strategy in boronic esters CANs and enhanced the
21 transesterification rate thanks to neighboring tertiary amines. This effect was latter implemented in
22 other kinds of vitrimers featuring ester or silyl ether exchangeable bonds for instance.^{38,45} In their
23 review, Guerre et al.⁴³ highlighted the few examples of internal catalysis in vitrimers reported so far,
24 and the strong potential of this strategy to tune the properties of vitrimers. More recently, Van
25 Lijsebetten et al.⁴⁶ also emphasized the power of NGP in dynamic covalent chemistry, especially in
26 polymeric materials, in a very clear and useful tutorial review. To go further on this concept, a
27 general outline of the activating groups potentially beneficial to vitrimers would give useful insight
28 for further research on this fast rising topic. Nevertheless, caution should be taken when using NGP
29 as this strategy can sometimes drastically modify the exchange mechanism.^{24,43} For instance,
30 transesterification which usually proceeds via an associative exchange, was reported to follow a
31 dissociative pathway in the presence of specific activating groups.^{47,48}

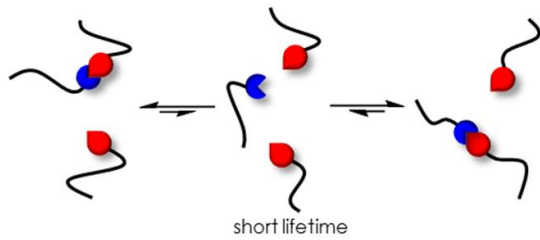
32 Activating groups are a very powerful yet complex tool. Because the case of vitrimer-like
33 dissociative CANs is still debated in the vitrimer community, this Perspective article focuses on
34 internal catalysis and NGP in associative exchange reactions, to follow the strict definition of
35 vitrimers.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

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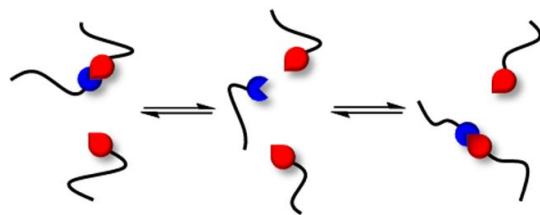


(A) Vitrimers



(B) Vitrimer-like CANs

$$k_{\text{dissociation}} \ll k_{\text{association}}$$



(C) Dissociative CANs

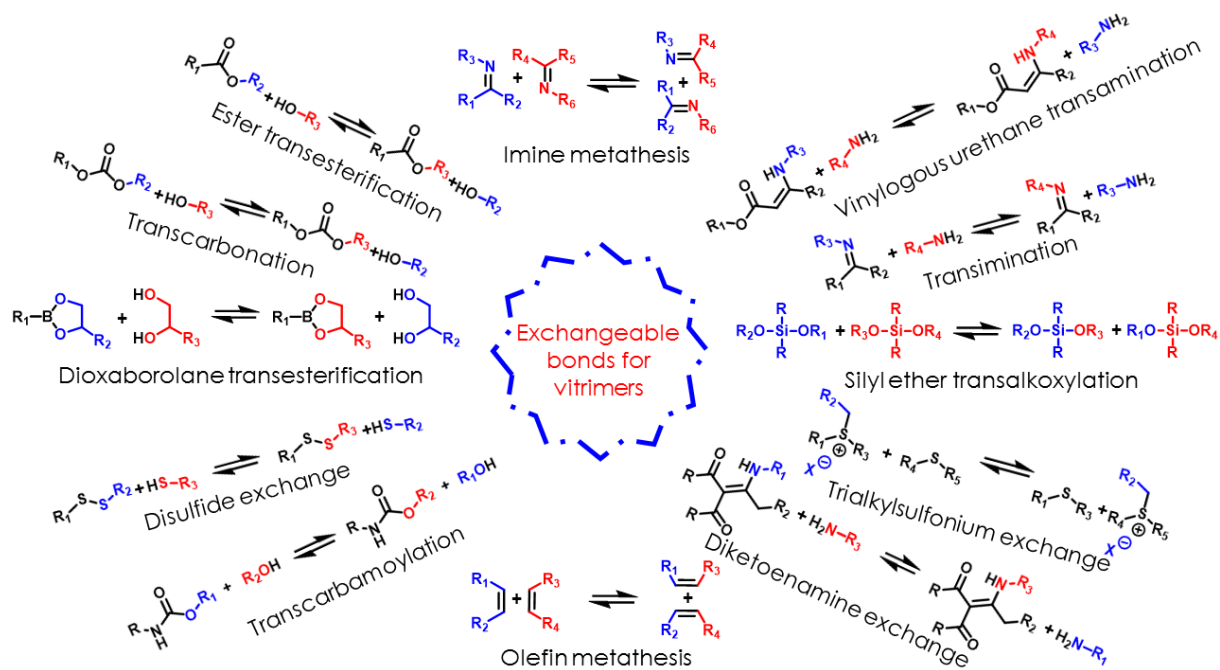
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3 *Figure 1. Schematic representations of the mechanisms at work in: A) associative CANs (vitrimers), B) Vitrimer-like*
4 *dissociative CANs and C) dissociative CANs. Vitrimer-like dissociative CANs (B) exhibit a constant K_{eq} over the vitrimer-like*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

6

1 (II) Exchangeable bonds with an associative mechanism

2



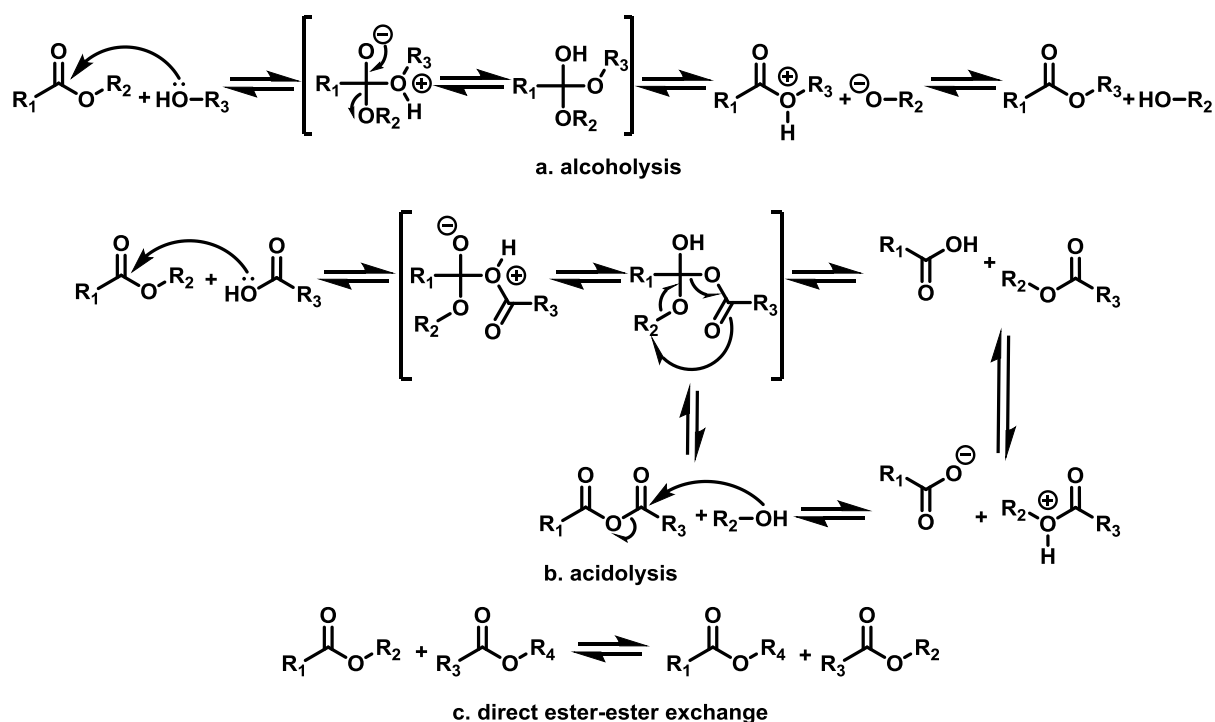
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4 Figure 2. Associative exchangeable bonds for vitrimers design.

1 Esters

2 Esters are probably one of the oldest known exchangeable bonds, as Friedel and Craft, famous for
3 the eponymous reaction, also discovered in 1865 the exchange reaction occurring between two ester
4 groups.⁴⁹ Several terms such as ester exchange, ester-ester interchange, transesterification or the
5 nowadays most commonly used transesterification are considered as synonymous, though they
6 actually encompass several reactions.⁵⁰ Actually three reactions are reported to happen in what is
7 commonly considered as the transesterification equilibrium,⁵¹ namely alcoholysis, acidolysis and the
8 genuine transesterification.^{49,52-54} Alcoholysis is the main reaction⁵⁵ although the direct ester-ester
9 exchange prevails for esters synthesized from aromatic acids over 300°C.⁵⁶ The alcoholysis
10 mechanism proceeds by the attack of the alcohol onto the carbon of the carboxylate. A tetrahedral
11 intermediate is thus formed prior to the elimination of an alkoxy group, leading either to the starting
12 ester or to the exchanged one (Scheme 1a).

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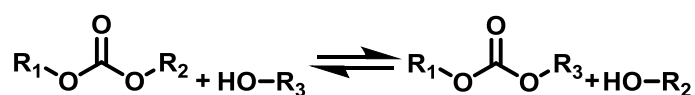
16 *Scheme 1. Ester exchange mechanisms a. alcoholysis, b. acidolysis and c. direct ester-ester exchange.*

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

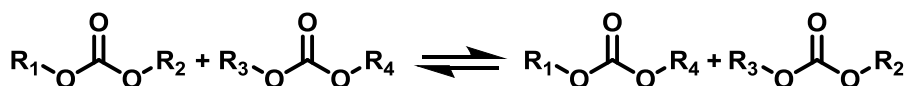
1 among scientists with the development of biodiesel and biofuels. Recently, the interest in biomass
2 valorisation and greener fuels has grown and catalysts such as *N*-heterocyclic carbenes,⁶¹ calcium
3 oxide,⁶² ZrO₂/SO₄,⁵⁹ silicates and clays^{63,64} or aluminum chloride⁶⁵ were (re)discovered. Metal-based
4 catalysis (such as Sn, Ti or Mg^{51,54} for instance) draws particular attention as zinc-based catalysts
5 were recently used in the first reported vitrimer.¹ The mechanism involves a Zn²⁺ species, which
6 coordinates to the ester carbonyl group and activates it with respect to the nucleophilic attack of the
7 alcohol or alkoxide, and then proceeds via the pathway previously described.⁶⁶ In summary, all the
8 catalytic mechanisms encountered so far were associative.

9 Carbonates

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



a. transcarbonation



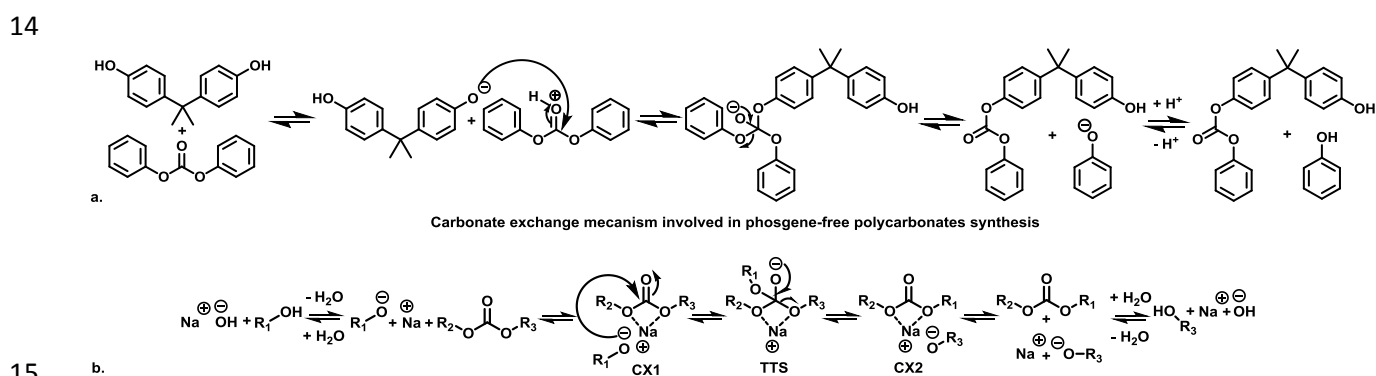
b. carbonate interchange

16

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

18

1 The interest for transcarbonation rose when scientists aimed at synthesizing polycarbonate materials
 2 without the use of highly toxic phosgene.⁶⁷ The exchange between diphenyl carbonate and bisphenol
 3 A was used as a safer pathway to produce polycarbonates. The mechanism involved was similar to
 4 ester transesterification⁶⁸ and was proven quite recently. In the absence of catalyst, there is a
 5 prototropy between the phenol and the carbonate. The deprotonated counterpart (phenolate) is the
 6 reactive species towards the electrophilic carbon of the carbonate carbonyl moiety. The reaction
 7 proceeds through a tetrahedral intermediate before the elimination of a phenolate (from the starting
 8 carbonate or from the reactant).^{69,70} However, this exchange is very slow.⁶⁷ Transcarbonation is
 9 known to be catalyzed by metal-derived catalysts such as tin salts,⁷¹⁻⁷³ zinc acetate,⁷⁴ copper salts,⁷²
 10 and even a dimetallic iron-manganese cyanide catalyst.⁷⁵ Bases are also common catalysts, for
 11 instance magnesium hydroxide,⁷⁶ calcium salts^{77,78} or sodium alkoxides.^{74,79} All the catalyzed
 12 mechanisms described are associative,^{69,71,74,76-80} though they are slightly different depending on the
 13 type of catalysis employed (Scheme 3).



15
16
17 *Scheme 3. a. transcarbonation pathway and b. catalytic effect by bases and metal ions.*

18

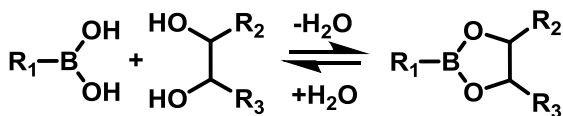
19 When a base catalyst is used, the carbonate and the alcohol moiety are presumably hydrogen
 20 bonded in a pre-reaction complex (CX1). Then the reaction proceeds via a tetrahedral transition state
 21 (TTS) yielding a post-reaction complex (CX2) and ultimately the free exchanged species (Scheme
 22 3b).⁷⁴ The overall reaction follows an “addition-elimination” mechanism. When a Lewis acid catalyst
 23 is employed, such as zinc acetate, a cyclic transition state involving a ternary complex between the
 24 carbonate, the alcohol and the catalyst is formed. Then, the reaction proceeds through a concerted
 25 mechanism to generate a post-reaction complex, following an addition/elimination mechanism.⁷⁴
 26 Direct ester-carbonate interchange have also been reported⁸¹ and described as following an
 27 associative pathway as well.

28

29 **Boronic esters**

30 Cyclic boronic esters, also known as dioxaborolanes are synthesized by condensation of boronic acids
 31 with 1,2- and 1,3-diols leading to 5- and 6-membered rings respectively.⁸²⁻⁸⁴ Boronic acids are used in
 32 a wide range of reactions in organic chemistry, as catalysts, pronucleophiles (cross-coupling
 33 reactions) or reaction intermediates.^{82,85} In carbohydrate chemistry, they are also useful as protective
 34 groups for diols and diamines.^{82,85,86} Besides, their ability to bond with diols makes them particularly
 35 useful in biology, biochemistry or chromatography for sugars and diol-bearing compounds
 36 purification or carbohydrates sensors for example.^{85,87-89} In medicine they are also proposed for drug
 37 delivery⁹⁰⁻⁹² and glucose sensing for diagnostic purposes.^{93,94} The key feature of boronic esters is their

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



6

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

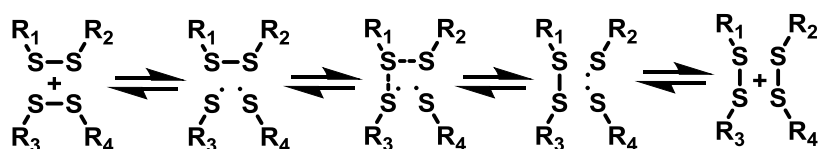
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9 Over the past few years, growing interest for this functionality has spread in the polymer science
10 community, in particular for the preparation of self-healing polymers.^{100,101} Interestingly, Sumerlin et
11 al.¹⁰¹ showed that two different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

28 Sulfur-containing bonds

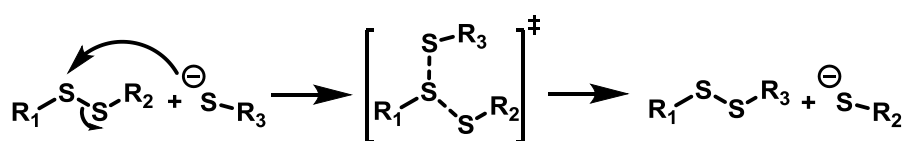
29 Disulfides

30 For a long time, disulfide bonds have been known to feature an interesting reversible behaviour.
31 Historically, this behaviour has been used in personal care products. Disulfide bonds naturally
32 occurring in keratin were cleaved by a reducing agent before new bonds were generated using an
33 oxidant to perform so-called "permanent wave" on hair.¹⁰⁶ This process can be considered as an early
34 chemically-reshapable material and was implemented after several decades in reversibly crosslinked
35 polymers.^{107,108} Disulfide bonds are also involved in the rubber vulcanization process. Hence, in 1946,
36 Stern and Tobolsky already discussed possible mechanisms for the reshuffling of these bonds to
37 explain stress relaxation in these materials.¹⁰⁹ The mechanism remained uncertain but usually
38 admitted to be associative.¹⁰⁴ Two possible mechanisms have been discussed: 1) a [2+2] metathesis
39 mechanism, and 2) a radical-mediated [2+1] mechanism, where a S-S bond would be homolytically
40 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.



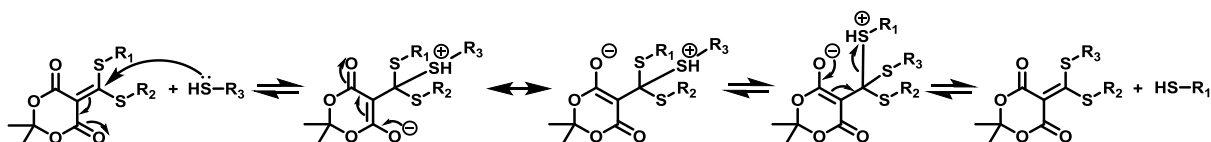
Scheme 6. Thiol-disulfide exchange mechanism.

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

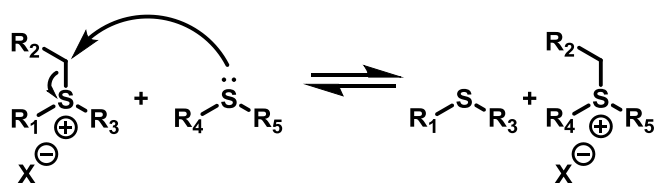
Sulfur-bearing Meldrum's acids were also described as exchangeable crosslinkers in PDMS vitrimers through an associative mechanism involving thiol moieties (Scheme 7).¹¹⁹



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

1 *Trialkylsulfonium salts*

2 In the 1970s, a group at Ghent got interested in poly(propylenesulfide) and the mechanism of its
3 degradation upon incorporation of oxonium salts to introduce sulfonium groups in the material. They
4 reported an exchange reaction between thioethers and trialkylsulfonium likely proceeding through
5 an associative mechanism whereby the sulfur atom of the thioether attacks the α -carbon atom of a
6 sulfonium salt prior to the elimination of the exchanged thioether following an associative pathway
7 (Scheme 8).¹²⁰⁻¹²³ The fact that sulfides react with electrophiles (brosylates for instance) and the
8 positively charged sulfonium is a good leaving group comfort the hypothesis of a S_N2 mechanism,
9 while a S_N1 is unlikely considering this pathway would involve a highly unstable primary carbocation.
10 Four decades later, the group of Du Prez studied and updated this forgotten chemistry and
11 implemented it in polythioether networks to prepare catalyst-free vitrimers.⁴⁰ Knowledge on this
12 bond exchange chemistry remains scarce, but the promising opportunities offered in rubber
13 recycling¹²⁴ might favor more in-depth studies.



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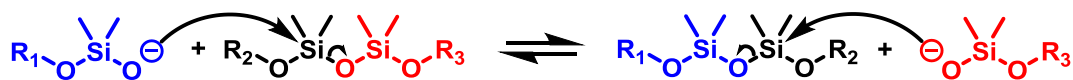
15 *Scheme 8. Proposed mechanism for thioether-sulfonium exchange.*

16

17 *Silyl ether transalkoxylation and metathesis*

18 Silicones represent an \$11-billion industry and production of formulated silicones exceeded 2Mt in
19 2013.¹²⁵ Silicones are made from silicon, which is also the main component of glass. In the 1950s,
20 polydimethylsiloxanes (PDMS) were reported to exhibit stress relaxation behaviour thanks to a
21 chemical phenomenon of chain exchange, catalyzed either by an acid or a base.^{126,127} The acid-
22 catalyzed mechanism was supposed to involve a protonated oxygen atom on the Si-O-Si bond as an
23 intermediate,¹²⁷ but this mechanism still seems unclear. The base-catalyzed mechanism was
24 supposed to involve the attack of the basic species onto a silicon atom consequently cleaving a Si-O-
25 Si bond and yielding an anionic ⁻O-Si group.¹²⁷ However, the mechanism leading to the exchange
26 between two polymer chains was not fully elucidated. Surprisingly, the self-healing properties of
27 these materials were somehow forgotten, except for a patent reporting thermally reversible silicone
28 rubbers catalyzed by strong acids, becoming malleable at 150 °C but remaining insoluble and
29 dimensionally stable at room temperature.¹²⁸ The self-healing behavior of polysiloxanes was
30 rediscovered in 2012 by McCarthy et al.¹²⁹ after the concept of vitrimer was first defined. They
31 studied tetramethylammonium dimethylsilanolate-terminated polysiloxane chains and emphasized
32 that any crosslinked PDMS elastomer could be converted into a self-healable polymer by addition of
33 basic catalysts. The mechanism involved is an associative trans-siloxanation. The first step of this
34 mechanism would be the dissociation of the chain-end silanolate-counterion ion pair followed by the
35 attack of the silanolate anion onto a silicon atom and simultaneous cleavage of a Si-O bond (Scheme
36 9).^{130,131} Thus the ion pair would behave as a dormant species, and the silanolate anion as the active
37 one enabling chain exchange. Other strong bases can be used to generate living chain ends such as
38 the most effective potassium hydroxide and cesium hydroxide, but a major flaw at high temperature
39 is the formation of volatile cyclic oligomers leading to decreases of connectivity and average molar
40 mass.¹³¹ In 2017 Guan et al. used a silyl ether as the exchangeable moiety in crosslinkers to make
41 polystyrene networks, where the exchange reaction involved free hydroxyl groups without ion
42 pairs.⁴⁵ Finally, the same group reported an exchange reaction in the absence of free hydroxyl

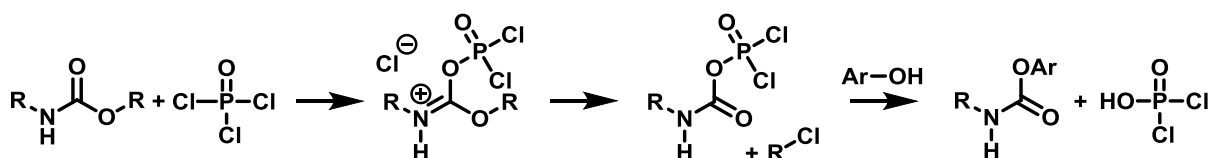
1 moieties and hypothesized a direct silyl ether metathesis mechanism catalyzed by acids, but the
 2 mechanism still remains unclear and further investigations are needed to fully understand the
 3 behaviour of this material.¹³²



5 *Scheme 9. Trans-siloxanation mechanism.*¹³⁰

6 Urethanes, ureas, thiourethanes and hydroxyurethanes

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



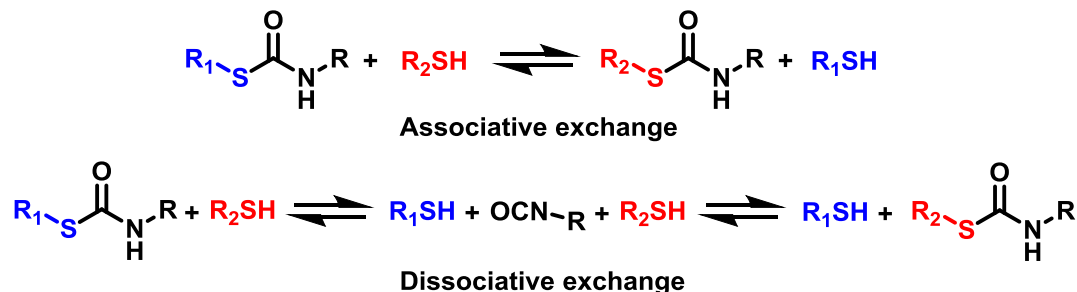
28 *Scheme 10. Phosphoryl chloride as a catalyst favors the associative mechanism of transcarbamoylation with phenols.*¹⁴⁰

30

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

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

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

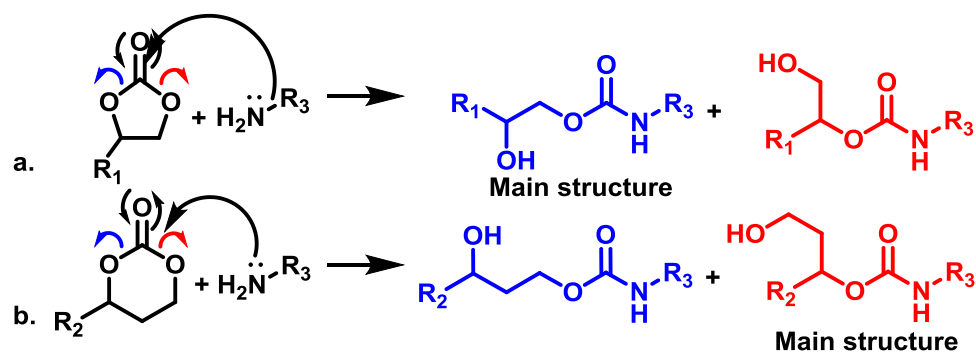


6

7 *Scheme 11. Associative and dissociative exchange pathways for polythiourethanes.*^{144,145}

8

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

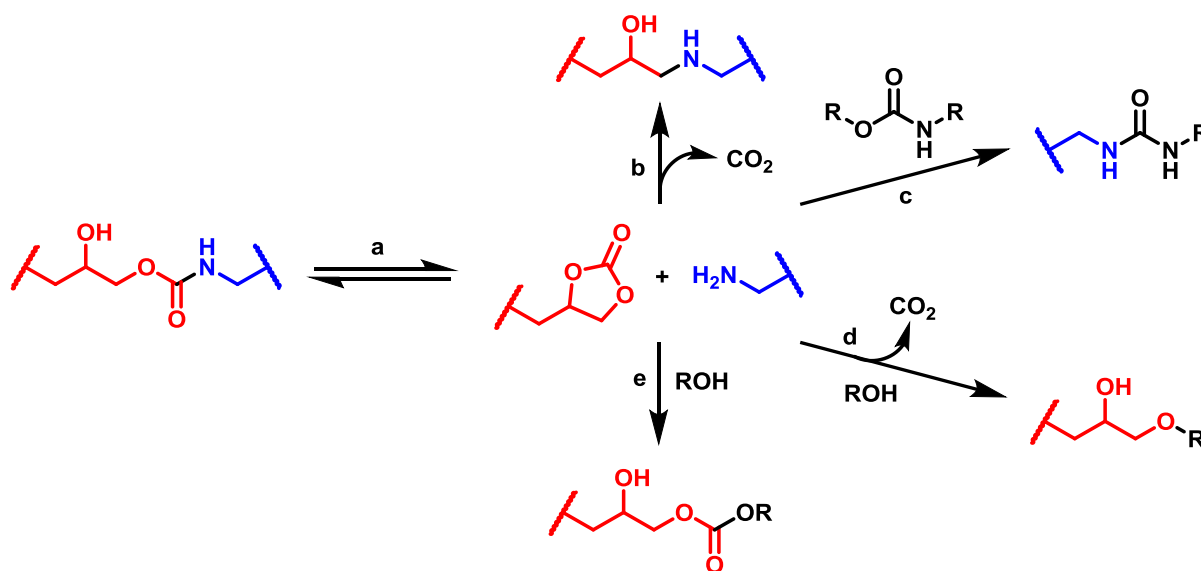


14

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

17 Fortman et al. studied PHU vitrimers and suggested that transcarbamoylation occurred, albeit slowly,
 18 and that decomposition and side reactions occurred more easily at high temperatures.¹⁴⁶ In
 19 particular, side reactions were observed at 160 °C and over, whereas the decomposition of the
 20 urethane linkage to an isocyanate and an alcohol usually occurs over 250 °C. These observations
 21 were highly dependent on the type of PHU: 5-membered cyclocarbonates-derived PHU (5-CC PHU,
 22 Scheme 12a) were more prone to decomposition *via* dissociative reactions at 180 °C. 5-CC PHU were
 23 shown to decompose back to their 5CC amine precursors (Scheme 13a). Several decomposition
 24 reactions were hypothesized: reaction of amine with cyclic carbonates by irreversible
 25 decarboxylative mechanism (Scheme 13b), addition of amines to carbamates to form ureas (Scheme
 26 13c), decarboxylative reaction of free hydroxyl groups with cyclic carbonate to form ethers (Scheme
 27 13d) or carbonates (Scheme 13e), and oxazolidone formation, to name a few. These irreversible
 28 reactions are responsible for the loss of mechanical properties of the reprocessed materials. On the
 29 contrary, the dissociative reversion reaction leading to the starting amine and cyclocarbonate was
 30 not observed for 6-CC PHU (Scheme 12b), thus limiting the decomposition reactions. This suggests

1 that the associative transcarbamylation may be responsible for the stress-relaxation behaviour
2 observed for these 6-CC PHU materials.^{139,147}



3
4

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

7

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

16

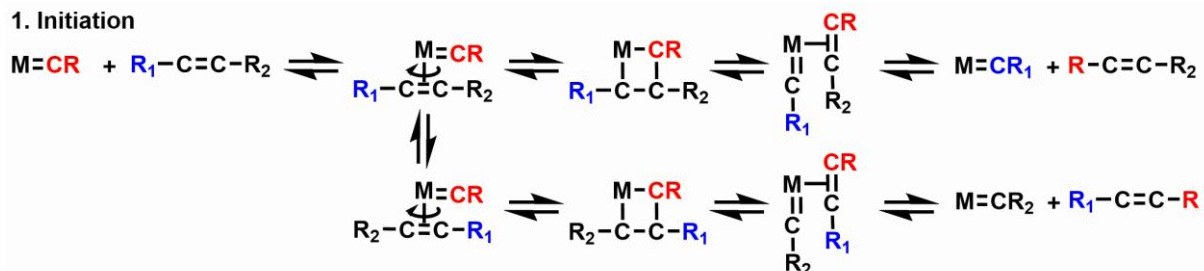
17 Olefin metathesis

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

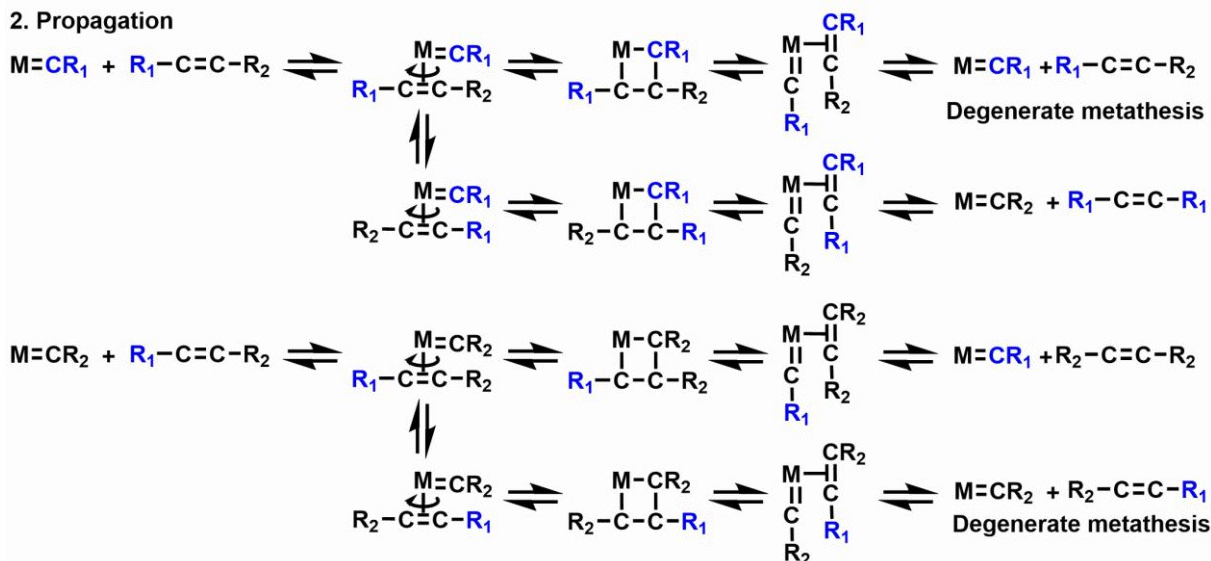
1 the steps for this reaction are equilibria, so if the reactants and desired exchanged products have a
 2 similar enthalpy, the reaction is degenerate. This property is convenient to make exchangeable
 3 crosslinks in vitrimers. In contrast, when metathesis is used for organic synthesis, aiming at efficient
 4 synthesis of a desired exchanged olefin product, the equilibrium can be easily displaced by using a R-
 5 CH=CH₂ olefin as the substrate. Thereby, the direct reaction yields the desired product and easy
 6 removal of ethylene from the reaction vessel provides the necessary driving force for the reaction to
 7 happen preferentially in the desired direction. An example of polybutadiene vitrimers implementing
 8 olefin metathesis as the exchange reaction was reported.^{160,161} These materials were made of
 9 crosslinked polybutadiene by reaction of butadiene with benzoyl peroxide. The interest of
 10 polybutadiene is the presence of insaturations in the network after crosslinking. These insaturations
 11 can undergo olefin metathesis in the presence of a Grubbs catalyst. Therefore, it is possible to make
 12 a vitrimer by adding a Grubbs second-generation catalyst before the polymerization, but a much
 13 more original approach is to make a vitrimer out of a thermoset by swelling it with a solution of the
 14 catalyst after the crosslinking process. Such strategy to make vitrimers has so far been specific to
 15 olefin metathesis vitrimers. These vitrimers exhibited self-healing at ambient temperature and
 16 below. Self-healing behavior was also observed for thermoset materials after the catalyst was only
 17 applied on the surface where healing was required. When no catalyst was used, no effective self-
 18 healing was observed. In summary, olefin metathesis allows original strategies to make vitrimers,
 19 which is not possible with other chemistries. However, the use of a metal catalyst seems unavoidable
 20 and could be seen as the major drawback of this exchange reaction.

21

1. Initiation



2. Propagation



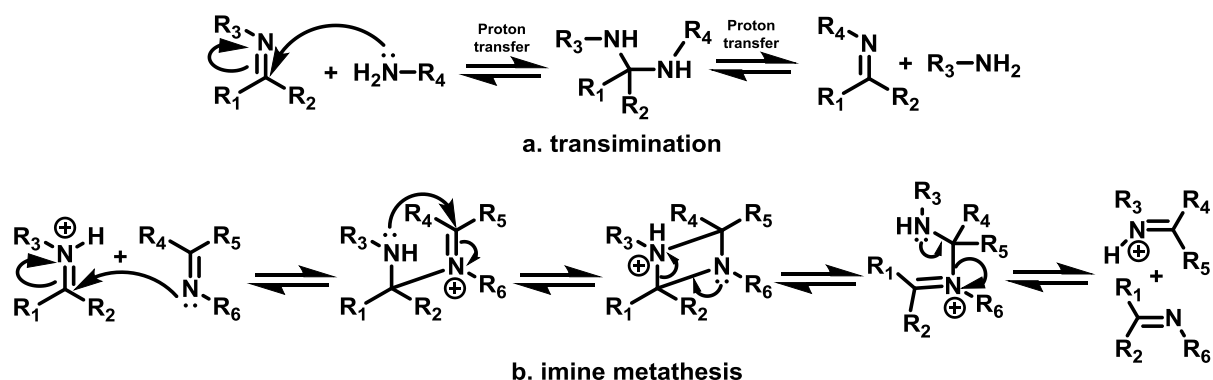
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23 Scheme 14. Olefin metathesis mechanism.¹⁵⁰

1 Imines

2 Imines result from the condensation of an aldehyde or a ketone and a primary amine to obtain a C=N
3 bond. Imines were investigated in the field of biochemistry, as their reversible covalent bond is
4 known to be involved in enzymatic reactions,¹⁶² and more recently in the field of materials
5 chemistry,¹⁶³⁻¹⁷⁵ with the growing interest in dynamic covalent networks. Actually three exchange
6 reactions are known for imines : a dissociative hydrolysis followed by reaction with another amine;
7 an associative exchange between an imine bond and a free amino moiety called transimination;
8 and a direct associative imine-imine exchange referred to as imine metathesis.^{166,170} Obviously, only the
9 latter two associative reactions are interesting for associative CANs design. Although dissociative
10 hydrolysis may happen in imine-based vitrimers, if the amount of water in the polymer matrix
11 remains low, this reaction is unlikely to influence significantly the properties of the material.
12 Therefore, the focus here is put on transimination, which requires residual amines, and on imine
13 metathesis, which does not. Transimination has been known to occur through an equilibrated
14 associative pathway for several decades.^{176,177} Three successive steps were described. The first and
15 rate-determining step consists in the attack of a free primary amine on the imine carbon atom to
16 form a geminal diamine tetrahedral intermediate.^{162,178-181} Then, two protons transfer from the
17 nitrogen atom of the formerly attacking amino moiety to the nitrogen atom of the formerly imine
18 moiety.^{162,179,181} Finally the exchanged amino moiety dissociates and leads to the formation of the
19 new imine.¹⁶² (Scheme 15a) The mechanism of imine metathesis is less extensively studied, but is
20 described as a nucleophilic addition of a neutral imine to a protonated one. The reaction proceeds
21 through a 1,3-diazetidinium intermediate yielding the exchanged imines or the initial reactants.^{179,182}
22 (Scheme 15b) Transimination and imine metathesis have already been implemented in various
23 polymeric materials to make vitrimers directly from polyimines^{163,165,167,169} or using imine bonds to
24 crosslink polyesters,^{166,172,173,175} polybutadiene,^{164,168} polydimethylsiloxanes¹⁷¹ and polyethers.¹⁷⁴

25



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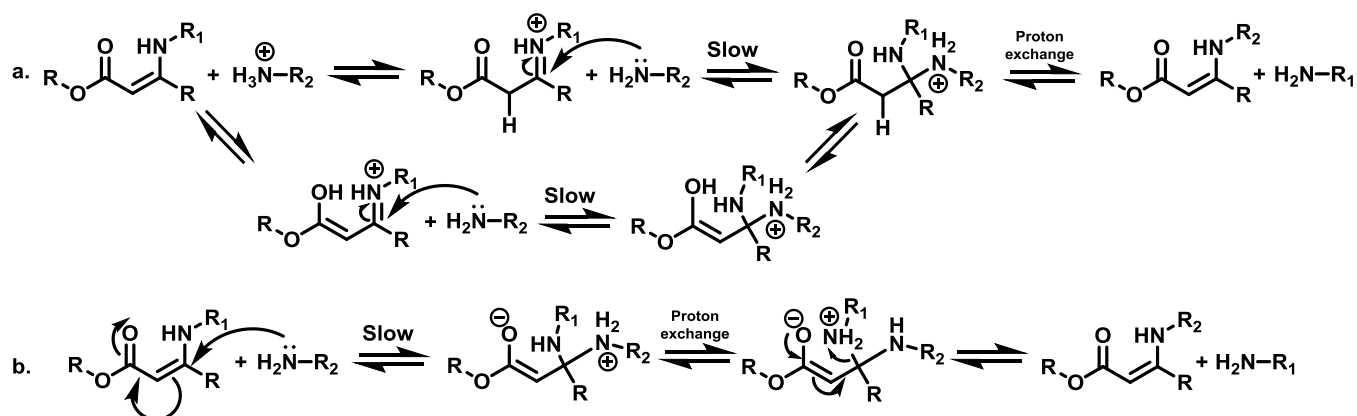
27 *Scheme 15. a. transimination and b. imine metathesis mechanisms.*

28

29 Vinylogous urethanes, ureas and amides

30 In the late 1970s, the exchange of amine moieties on enaminone structures was reported.¹⁸³ Later in
31 the 1990s, similar exchanges between dialkylamine-derived enaminones and aromatic primary
32 amines were discussed.^{184,185} However, this exchangeable bond was not been implemented in
33 polymers until 2014.¹⁸⁶ Moreover the mechanism involved in this first example was based on a
34 reversible hydrolysis to the amine and carbonyl components, although a possible “component
35 exchange” (amine direct exchange) was evoked by the authors. In this field of chemistry, enaminones
36 are commonly referred to as vinylogous urethanes, vinylogous ureas and vinylogous amides
37 depending on their structure. These structures are easily prepared by acetoacetylation of polyols

1 followed by reaction with a primary amine.¹⁸ In 2015 Denissen et al.¹⁸ reported the first vinylogous
 2 urethane vitrimer, exhibiting relaxation times as short as 85 s at 170 °C without the need of any
 3 catalyst. The exchange mechanism was later described by the same team¹⁸⁷ and depends on whether
 4 the medium is acidic, neutral or basic. In neutral and acidic conditions, the free primary amine is
 5 protonated to form an ammonium, and the ammonium-enamine couple is in equilibrium with the
 6 amine-iminium couple. The latter couple can evolve by reaction of the nitrogen atom of the amine
 7 with the iminium to form a geminal amine-ammonium tetrahedral adduct similar to the intermediate
 8 described earlier for transamination. Then, dissociation occurs, yielding either the exchanged
 9 products or the reactants (Scheme 16a). The amine-iminium pathway written in Scheme 16a
 10 (bottom) for a Brønsted acid can be extended to Lewis acids. Under these conditions, the reaction
 11 can proceed through a zwitterionic intermediate.



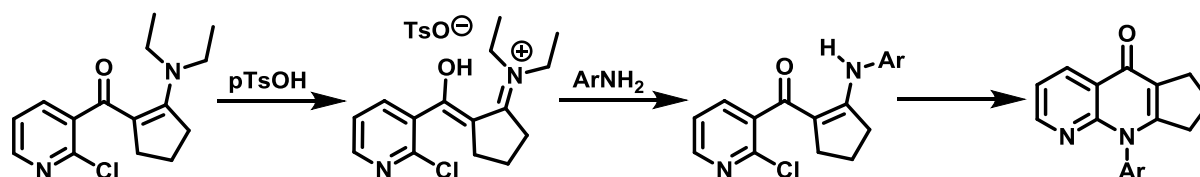
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14 *Scheme 16. Vinylogous urethane transamination mechanism a. in acidic and neutral conditions and b. in basic conditions.*

15

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

22
23



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

25

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

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

8 Catalysts also have an impact on the behaviour of vitrimers. The relaxation time of vinylogous
 9 urethane materials was reported to decrease from 10 mins at 120 °C in the absence of catalysts to 2
 10 min with 0.5 mol% of p-TsOH.¹⁸⁷ A recent study by Haida and Abetz¹⁹¹ studied the impact of p-TsOH
 11 in vinylogous urethane vitrimers with different stoichiometries. The networks were synthesized from
 12 hexane-1,6-diylbis(3-oxobutanoate) and tris(2-aminoethyl)amine (TREN). When an excess of amine
 13 was used, the relaxation time decreased from 29 s without p-TsOH to 0.3 s with 0.05 wt% p-TsOH.
 14 Similarly, with an excess of the acetoacetate the relaxation time decreased from more than 46800 s
 15 to only 134 s (Figure 3).¹⁹¹ DBTL and sulfuric acid were shown to be less effective. In the case of
 16 sulfuric acid, the sulfate anions probably form salts with the ammonium ions. In consequence, the
 17 ammonium species are less available, thus less reactive. Similarly, carboxylate anions are also known
 18 to be proton scavengers for ammonium species in non-aqueous solutions for instance.¹⁸⁷ When DBTL
 19 was used, the reaction activation energy dropped from 74 kJ.mol⁻¹ to 45 kJ.mol⁻¹ suggesting a
 20 different mechanism, probably via the carbonyl moiety activation of the vinylogous urethane. On the
 21 contrary, TBD increased the activation energy up to 103 kJ.mol⁻¹, because of proton scavenging.
 22 Interestingly Spiesschaert et al.¹⁹² managed to incorporate acidic or basic functionalized fillers in
 23 PDMS-vinylogous urethane matrices. When 10 wt% kaolin bearing acidic groups was incorporated,
 24 the relaxation time of the resulting material decreased from 5725 s to 4650 s at 150 °C, whereas non-
 25 functional fillers were shown to increase relaxation time. Acid, basic or neutral alumina fillers were
 26 also studied. When the relaxation time for the matrix was 4000 s, the material containing neutral
 27 alumina or basic alumina displayed relaxation times of 4650 s and 4500 s respectively. On the
 28 contrary, the material made from acid alumina showed a shorter relaxation time (3600 s), in
 29 agreement with the results observed in solution (Figure 4).¹⁹² Other kinds of catalysis were also
 30 reported and not surprisingly an excess of free primary amines in a vinylogous urethane vitrimer
 31 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

32
 33 *Figure 3. Impact of the stoichiometry and p-TsOH catalysis on vinylogous urethane properties.*^a ratio acetoacetate/amine^b
 34 *relaxation time at 110 °C*^c activation energy. (VU-E stands for an equal ratio of amines and acetoacetates, VU-A an excess
 35 *of acetoacetates and VU-NA an excess of amines).*¹⁹¹

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

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

4 Because they are versatile and they allow short reprocessing times, vinylogous urethanes have
5 already been implemented in various polymers networks. Many examples were reported such as
6 polysaccharide hydrogels,¹⁹³ polysiloxanes,^{188,190,192,194,195} polybutadiene,^{190,196} perfluoropolyether,¹⁸⁹
7 methyl methacrylate-(2-acetoacetoxy)ethyl methacrylate copolymer,¹⁹⁷ polystyrene,¹⁹⁸
8 polydimethylsiloxane (PDMS)-kaolin, PDMS-alumina and PDMS-aminated silica composites,^{188,192}
9 epoxy-amine copolymers,¹⁹⁹ polyethers¹⁹⁰ and vinylogous urethane polymers bearing
10 photodimerizable anthracene units.²⁰⁰

11



12

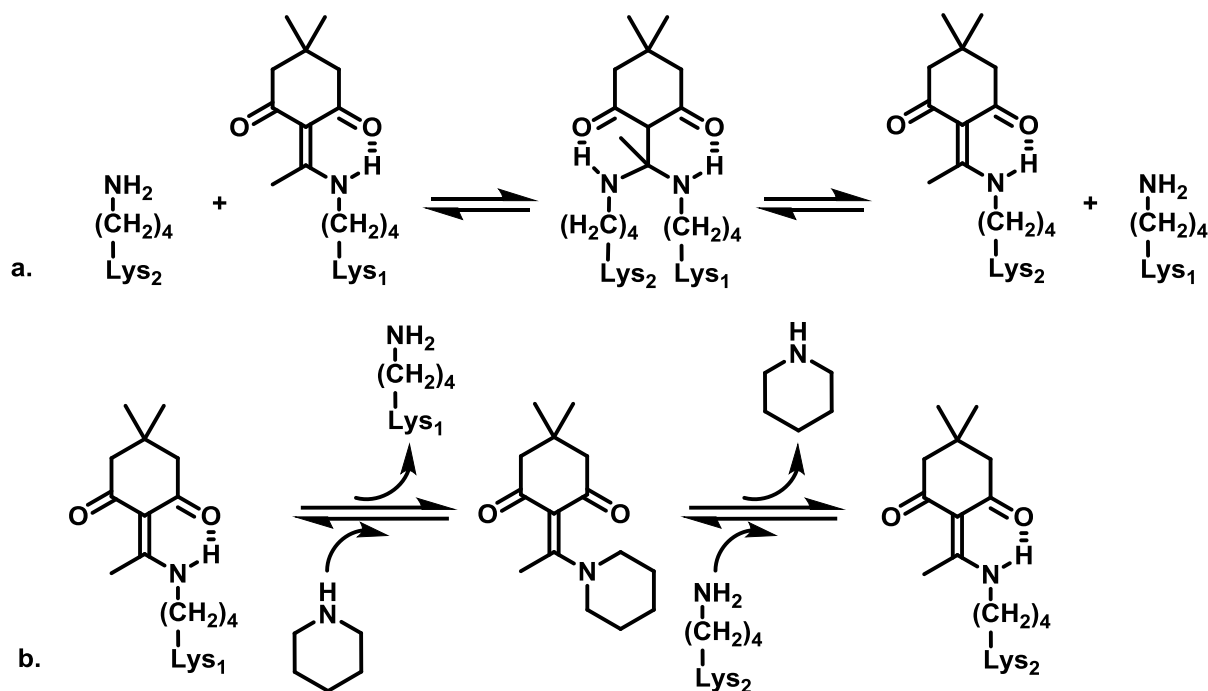
13 *Figure 4. Effect of different functionalization of alumina fillers on vinylogous urethane vitrimer composites relaxation time.*

14

15 Diketoenamines

16 Diketoenamines are known as Dde protecting group for amines in peptide synthesis.^{201,202} This
17 protecting group is formed by reaction between 2-acetyl-5,5-dimethyl-1,3-cyclohexanedione (also
18 known as 2-acetyldimedone) and primary amines.²⁰³ In 2009, the behaviour of Dde was studied in
19 detail on lysine in solid-phase synthesis. Lysine is an interesting amino acid bearing two amino
20 moieties, in α - and ϵ - positions.²⁰¹ This study reported the ability of ϵ -NH₂ to attack a Dde-protected
21 ϵ -NH₂ or α -NH₂ leading to an amine exchange. According to the authors,²⁰¹ the mechanism involves a
22 direct nucleophilic attack of the free amine on the Dde group via a Michael addition, before a retro-
23 Michael addition yielding either the original structure or the amine-exchanged one (Scheme 18a
24 Scheme 19).

1

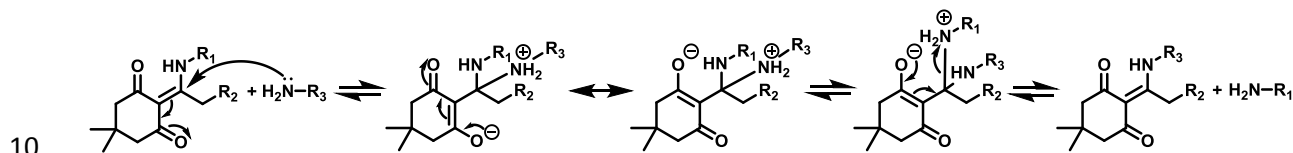


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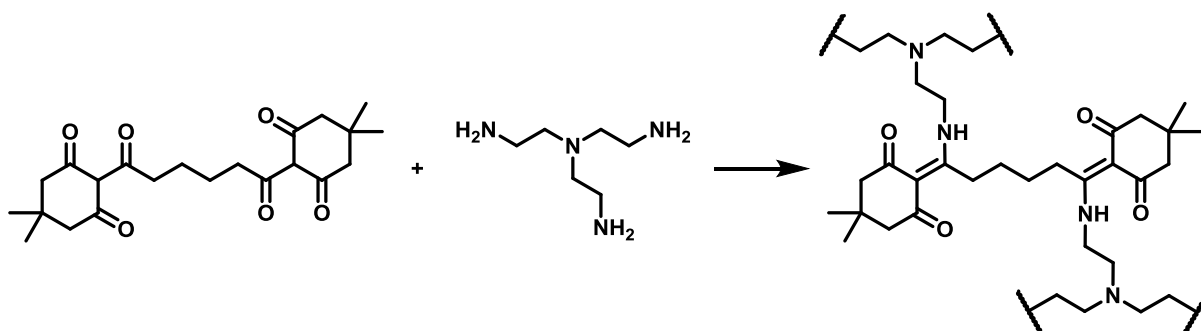
3 *Scheme 18. Dde protection group exchange on amines a. by direct electrophilic attack b. mediated by piperidine.*²⁰¹

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

9

11 *Scheme 19. Mechanism of diketoamines exchange.*

12 This chemistry was implemented in materials synthesis by Christensen et al to make vitrimers.^{204,205}
 13 who reported the synthesis of a network by click polycondensation between β -triketones and
 14 primary amines (Scheme 20). Triketones were synthesized from polytopic carboxylic acids and 1,3-
 15 diketones, and the final materials simply by ball-milling of the reactants at room temperature. The
 16 materials obtained were reprocessable without requiring a catalyst and followed an Arrhenius
 17 behaviour. These materials are easily hydrolysed. While this feature is often considered as a flaw, it
 18 can be beneficial for specific applications. In particular, as the materials are fully hydrolysed in a few
 19 hours at room temperature in sulfuric acid (less than 12 h in 5 M H₂SO₄), the monomers can be easily
 20 recovered. Amines are separated from the triketones thanks to an ion exchange resin, with a
 21 recovery above 90 %. The recovered monomers can be reused to make new poly(diketoamines).
 22 This feature affords a convenient and efficient chemical recycling by hydrolysis at room temperature,
 23 while other hydrolysable vitrimers require heating and more demanding conditions.

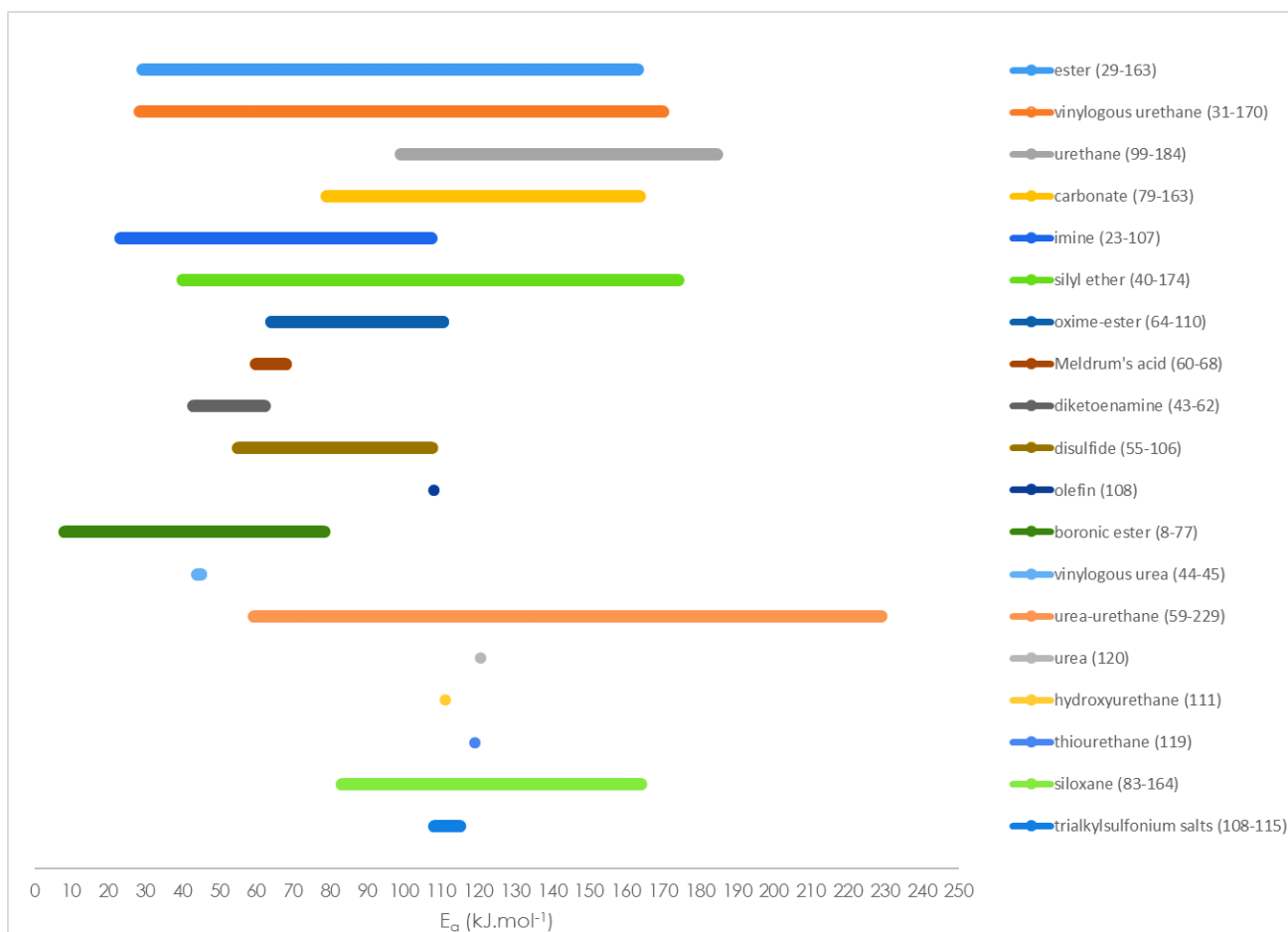


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3 *Scheme 20. Example of synthesis of diketoenamine vitrimer. Alternatively, various diketones and mixes of primary triamines*
4 *et diamines were also used.*^{204,205}

5

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



13

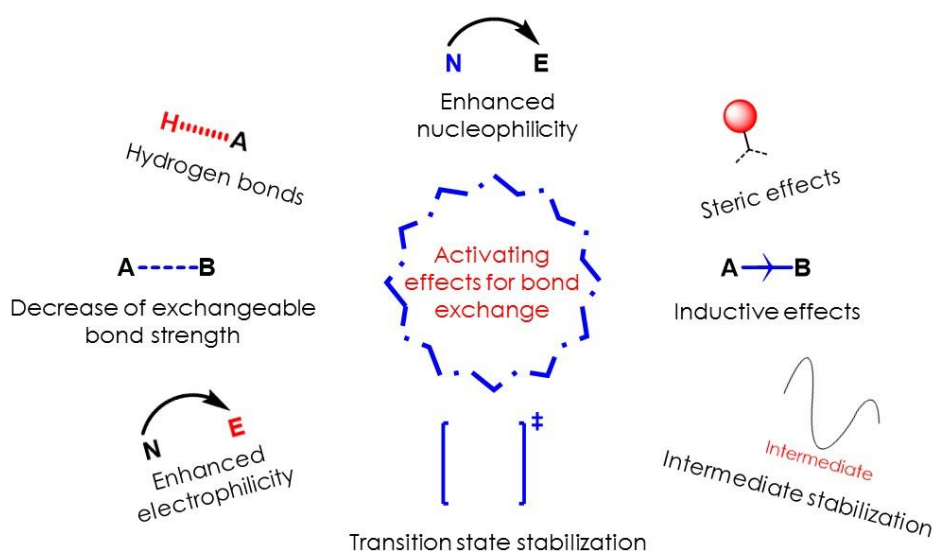
14 *Figure 5. Activation energy ranges for exchangeable bonds implemented in vitrimers.*

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.



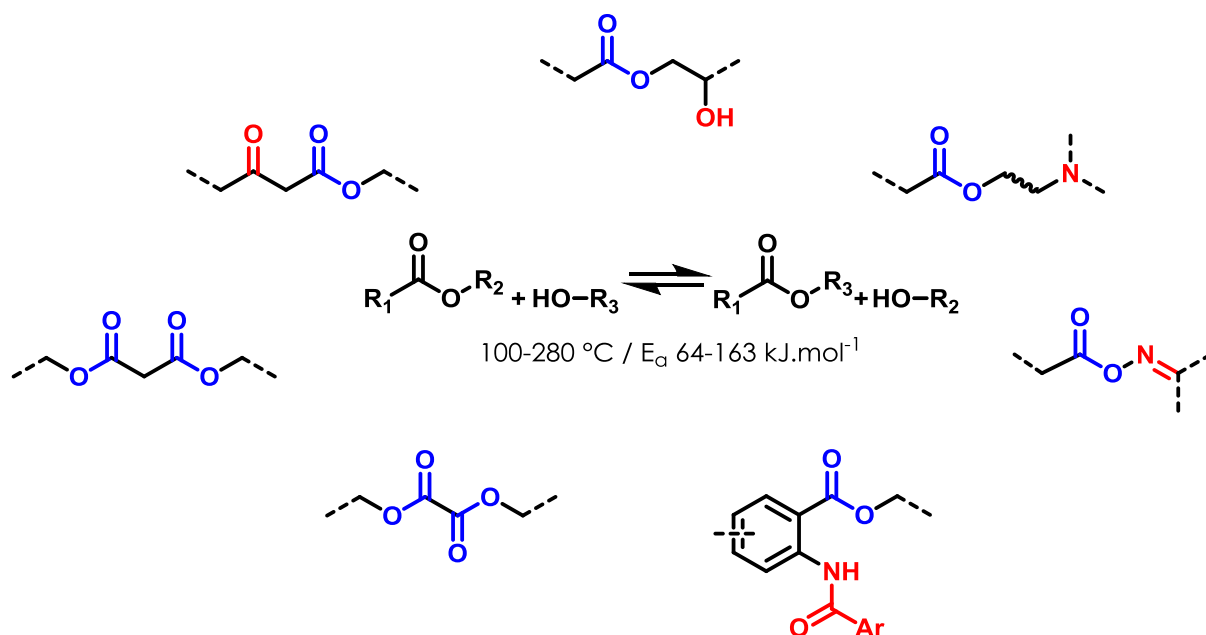
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15 *Figure 6. Examples of effects to activate bond exchanges.*

16

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

19

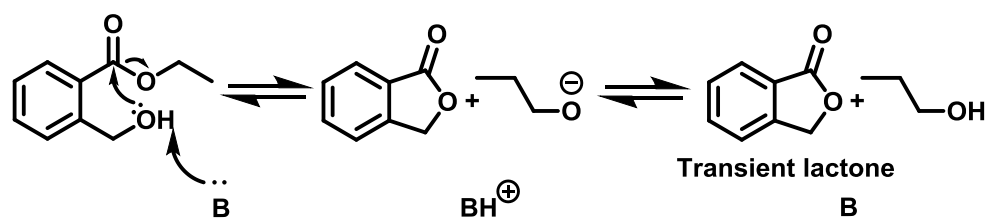


1
2

3 *Figure 7. Main examples of activating groups activating transesterification. The temperature range²⁵ for stress-relaxation*
4 *experiments and the range of calculated activation energies²⁴ of the exchange reaction in vitrimers are given.*

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

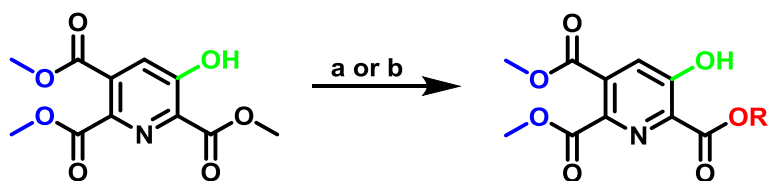
7 For instance, on phenyl esters, a neighboring hydroxymethyl group on the ortho position increases
8 the transesterification rate. However, the mechanism involves a cyclization after the attack on the
9 ester by the -OH group, leading to a transient lactone (Scheme 21).²⁰⁷



10

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

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

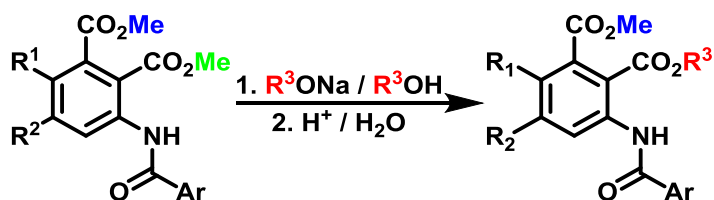


18

19 *Scheme 22. Regioselective transesterification: a) 10 mol% EtNiPr₂, ROH, 60 °C. b) 5 mol% Sc(OTf)₃, ROH, cat. H₂O, 60 °C.²⁰⁸*

1

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

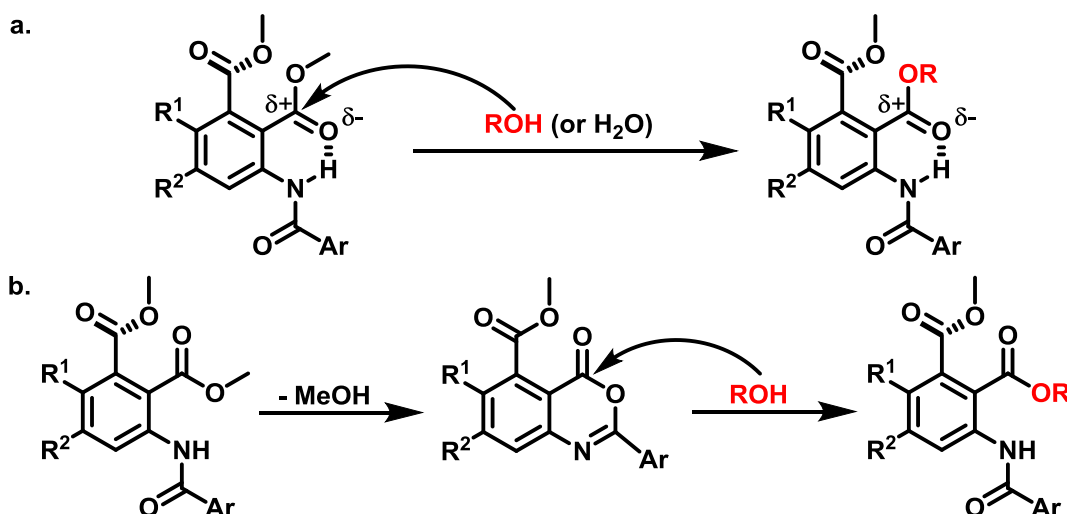


5

6 *Scheme 23. Regioselectivity of 3-benzamidophthalates transesterification.*

7

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

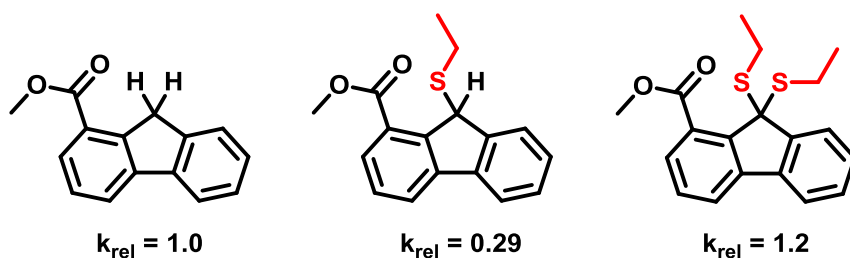


12

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

15

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

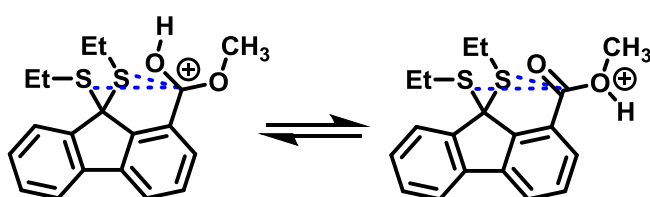


19

20 *Figure 8. Effect of substitution by ethylsulfane groups on fluorene esters transesterification rate.*²¹⁰

1

2 When one ethylthio group was present on the central 5-membered ring, the rate constant of
3 transesterification (using methanol-d₄) was 0.29 times the rate of the unsubstituted fluorene ester.
4 Interestingly, on the fluorene ester bearing two ethylthio groups, the effect was shown to be
5 opposite. This ester was more prone to transesterification. According to the authors of this study,²¹⁰
6 this phenomenon is likely due to at least two different causes resulting in opposite effects on the
7 transesterification rate. On one hand, the steric hindrance induced by one ethylthio group would
8 decrease the transesterification rate, as the reactive site is less accessible. On the other hand,
9 ethylthio groups induce a stabilizing electronic effect on the protonated ester intermediate (Scheme
10 25). The authors hypothesized that the electronic effect were low compared to the steric effect when
11 only one ethylthio substituent was present. On the contrary, when two ethylthio groups were
12 present, the resulting electronic effect is significant and exceeds the steric effect, even though this
13 effect is stronger than in the monosubstituted counterpart.

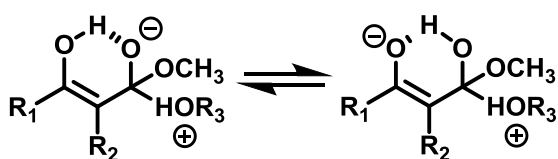


14

15 *Scheme 25. Stabilizing effect of sulfur on protonated esters.*²¹⁰

16

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



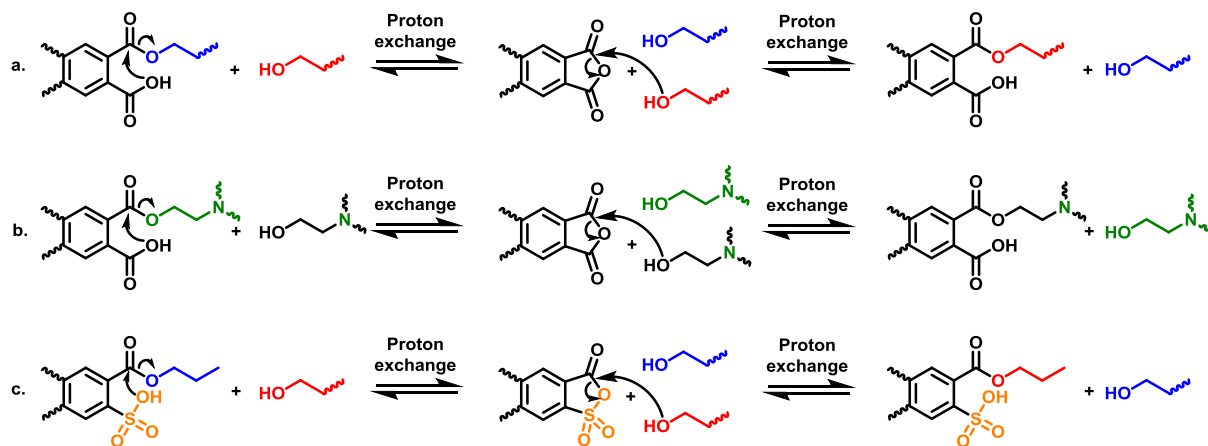
24

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

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

28 Phthalate monoesters also displayed enhanced transesterification similarly to the previously
29 discussed *o*-hydroxymethyl phenyl esters,²⁰⁷ as demonstrated by Du Prez et al.⁴⁷ The neighboring
30 carboxylic acid can indeed attack the carbonyl of the ester to yield a cyclic anhydride and an alcohol
31 (Scheme 27a). Recently the same team enhanced this effect by using a β -amino-diol with a
32 dianhydride to make networks (Scheme 27b). The enhancing effect of β -amines had already been
33 described for ester hydrolysis in 1962.²¹³ The tertiary amine at the beta position of the hydroxyl
34 groups induced a dual activation : the neighbouring group participation of the dangling -COOH and
35 the internal catalysis effect of the tertiary amine. The stress relaxation times decreased by a factor
36 500 compared to the amine-free analogous network.²¹⁴ However, it should be noted that the

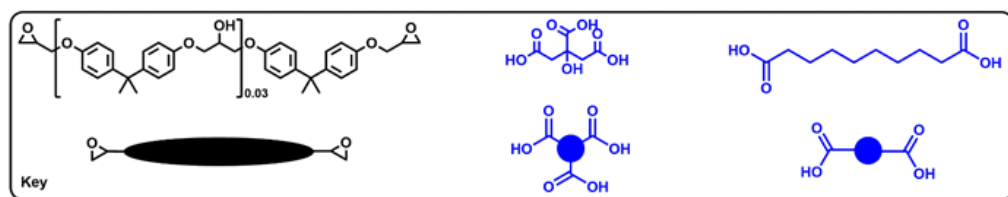
1 mechanism was dissociative in these cases, highlighting that great care should be taken when
 2 considering neighboring groups participation as they potentially change the bond exchange
 3 mechanistic pathway.^{47,214} The same mechanism was also recently reported with 2,5-bis(methoxy-
 4 carbonyl)benzenesulfonic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



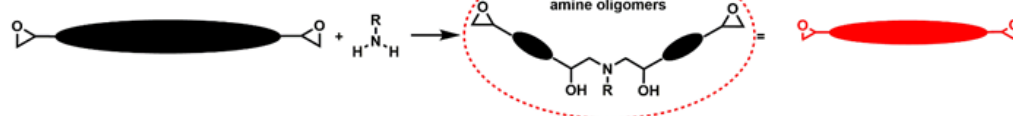
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7

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

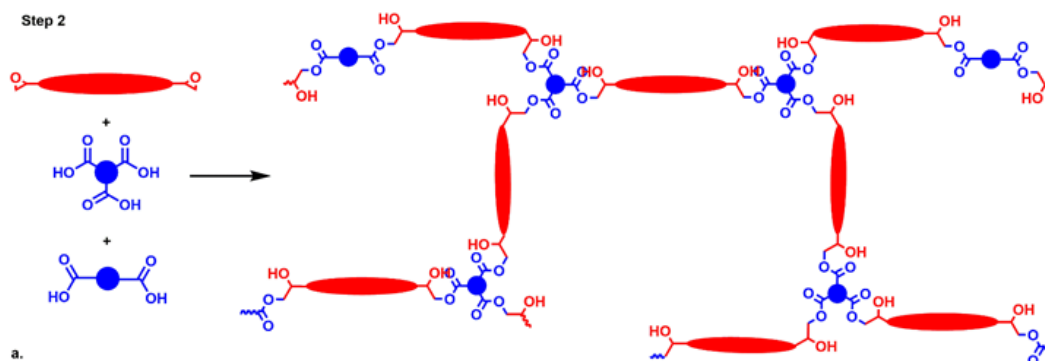
10 Amines were also shown to be efficient catalysts for transesterification vitrimers.¹⁷
 11 Triazabicyclodecene (TBD) in particular has often been used. Strategies have been designed to
 12 integrate tertiary amine groups into the polymer network. For example, bisphenol A diglycidyl ether
 13 (BADGE) was mixed with primary or secondary amines to generate epoxy-terminated tertiary amines
 14 oligomers. In a second step, the oligomers were reacted with polyacids to obtain a network bearing
 15 covalently-bonded tertiary amines (Figure 9a).³⁸ The exchange reaction activation energy (E_a) for this
 16 network was 93.6 kJ.mol^{-1} , very close to the $80\text{-}90 \text{ kJ.mol}^{-1}$ range observed for the Zn-catalyzed epoxy
 17 vitrimers. Alternatively, triethanolamine was added as co-reactant in a BADGE-(methyl nadic
 18 anhydride) system for the same purpose (Figure 9b).²¹⁶ The relaxation time at $190 \text{ }^\circ\text{C}$ decreased from
 19 19460 s to 4200 s when the triethanolamine content increased from 5 to 10 mol % (Figure 11).²¹⁶
 20 Recently catalyst-free transesterification vitrimers were synthesized from a hydrogenated dimerized
 21 acid derived from vegetable oil and tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM), a
 22 tetrafunctional epoxide bearing two tertiary amino groups (Figure 9c).²¹⁷ These tertiary amines were
 23 shown to act as internal catalysts. The effect was reported to be enhanced by the flexibility induced
 24 by the vegetable oil structure. Instead of increasing monomers flexibility, dangling chains which can
 25 plasticize the material, were also shown to promote similar enhancement as tertiary amines internal
 26 catalytic effect.²¹⁸ However, a similar internal catalysis was also reported in systems based on
 27 shorter, more rigid acids and which did not contain any plasticizer.²¹⁹ These examples of internal
 28 catalysis emphasize the role of tertiary amines as promising activating groups to increase
 29 transesterification rate.



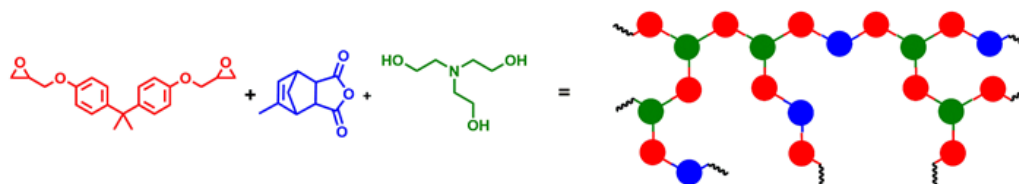
Step 1



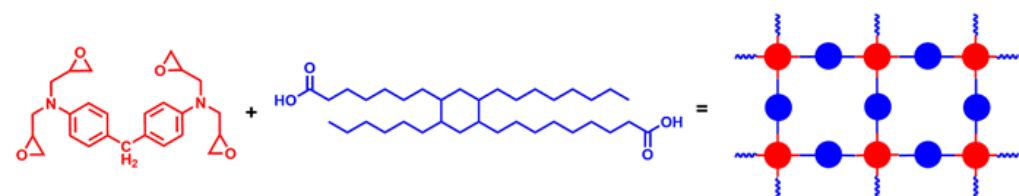
Step 2



a.



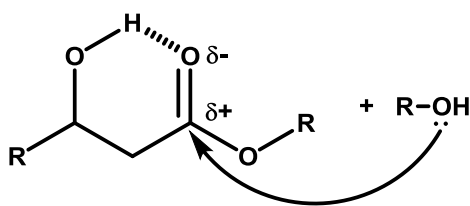
b.



c.

1
2 Figure 9. Strategies to embed tertiary amines in polyester networks using: a. epoxy-ended tertiary amines (2 steps),³⁸ b.
3 ethanolamine as co-reactant,²¹⁶ and c. a commercial tetraepoxide bearing tertiary amines.²¹⁷

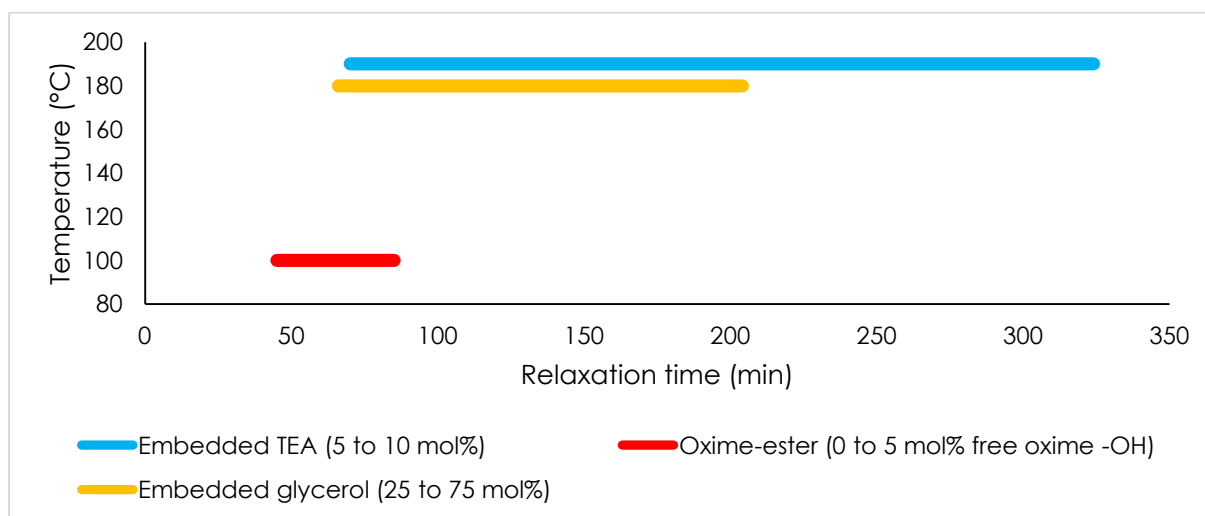
4
5 Interestingly, a chemistry similar to the first vitrimer¹ featuring β -hydroxyesters pointed out the
6 participation of the hydroxyl moiety in transesterification.^{34,220,221} A six-membered ring with a
7 hydrogen bond between the hydroxyl and the ester groups was hypothesized (Figure 10). The
8 hydrogen bond is assumed to weaken the ester bond as previously discussed for the 3-benzamido
9 group.



1
2 Figure 10. Hypothesized activating effect of the beta hydroxyl groups for transesterification. The hydrogen bond (dashed
3 bond) increases the carbonyl C electrophilicity, facilitating the attack of an electrophile such as an alcohol (first step of the
4 transesterification).

5
6 Besides, increasing the amount of free hydroxyl moieties was used to prepare catalyst-free
7 transesterification vitrimers.^{29,222} Although this effect cannot be considered as neighboring group
8 activation or internal catalysis, it remains significant in transesterification vitrimers, was often
9 reported in vitrimer literature, and therefore deserves to be mentioned. The acceleration of the
10 exchange reaction can be explained by the large amount of hydroxyl groups, facilitating the
11 transesterification by a concentration effect.^{33,219} In addition, a catalytic effect is also likely caused by
12 hydrogen bonding, as in the case of oxime-esters (vide infra). Accordingly, the addition of glycerol to
13 an epoxy-anhydride vitrimer matrix increases the concentration of free hydroxyl groups. The
14 concentration effect is clear as the relaxation time of the materials at 180 °C dropped from 204 mins
15 to 86 and 66 mins for 25 mol% 50 and 75 mol% of glycerol respectively (Figure 11).³³

16
17

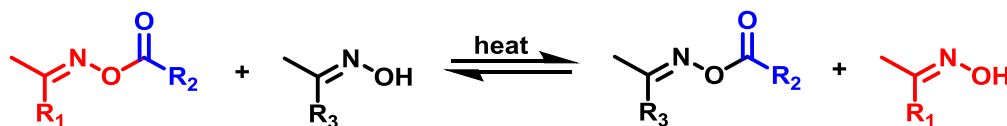


18
19 Figure 11. Effect of various enhancing strategies on stress relaxation time: hyperbranched epoxy prepolymers (HBE),
20 network-embedded triethanolamine (TEA) and free oxime hydroxyl group in oxime-ester network.^{33,216,233} Note that
21 comparison between these 3 systems should be exerted with caution since structural parameters (backbone, crosslinking
22 density...) differ from one system to the other..

23 The case of oxime-esters

24 Oxime-ester bonds can be considered as a subgroup of the ester family, or as a specific type of bond.
25 The most important difference between oxime-ester and ester is the nucleophile (an oxime instead
26 of an alcohol). Heat-induced transesterification of oxime-ester enabled the synthesis of catalyst-free
27 vitrimers (Scheme 28),²³³ with relaxation times ranging from 5102 to 2725 s at only 100 °C,
28 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

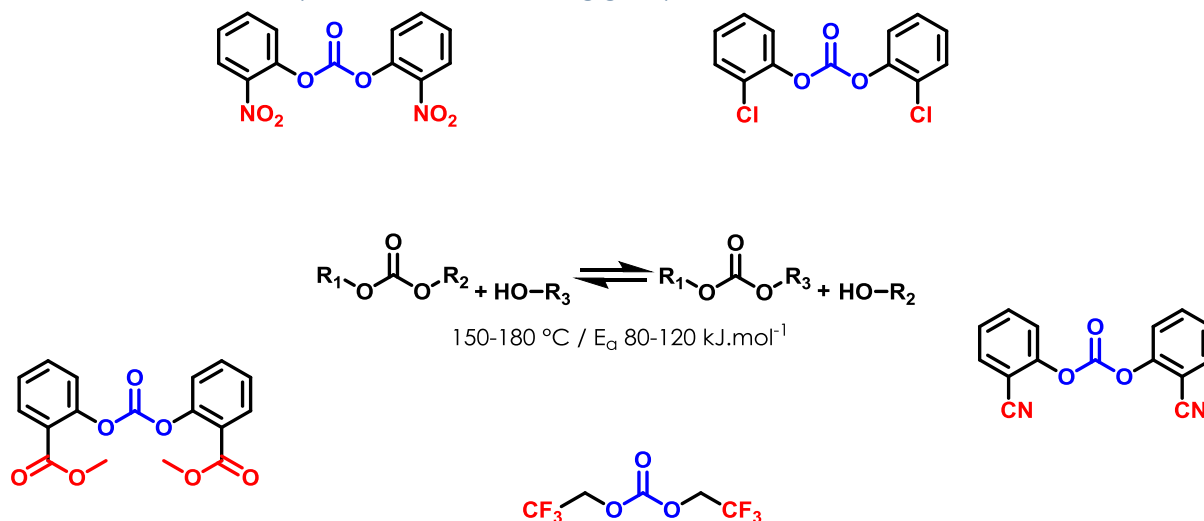
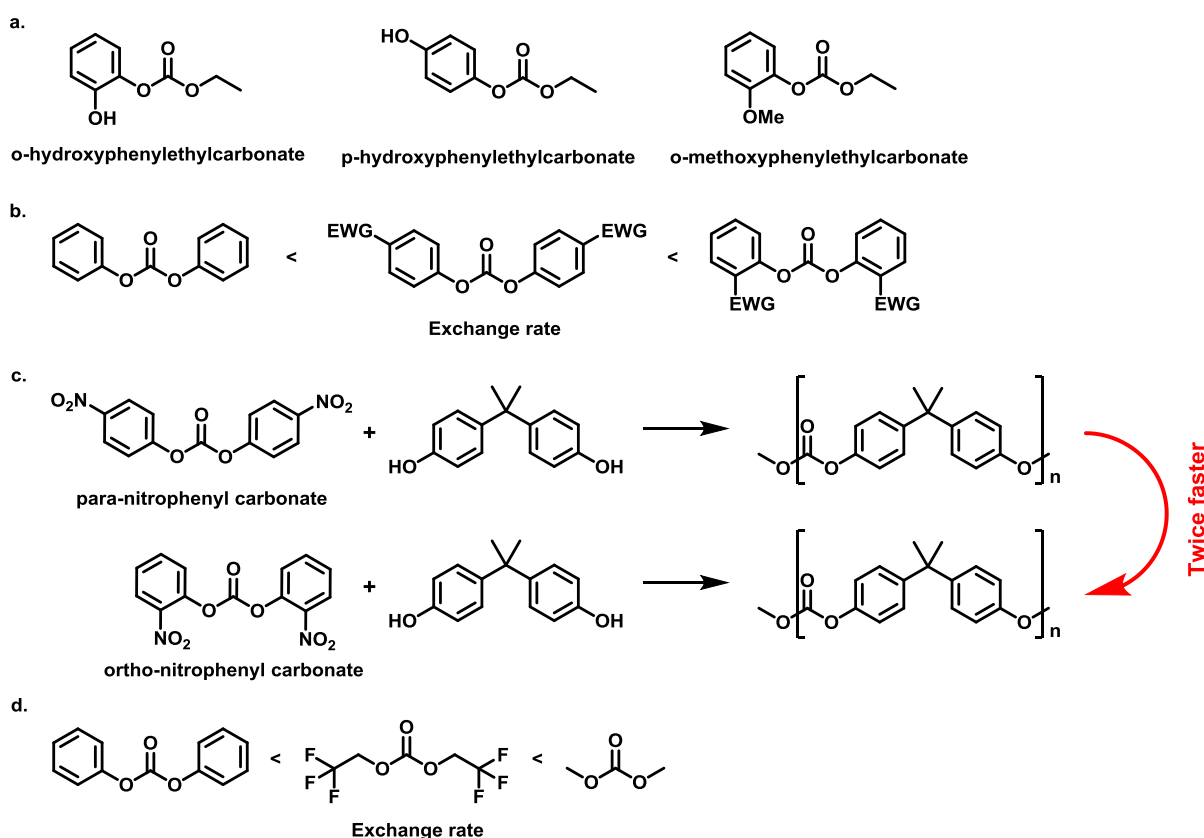


Figure 12. Examples of activating groups enhancing transcarbonation rate in solution and characteristics of reported transcarbonation vitrimers.²²⁵⁻²²⁸

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*-

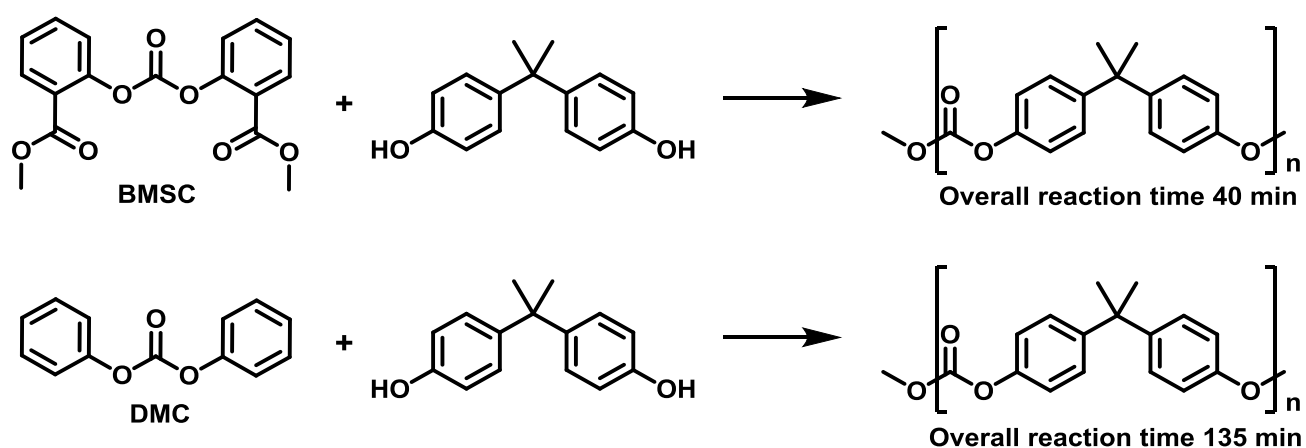
1 hydroxy- and *o*-methoxy- substituted compounds were not significantly different. However, in
 2 neutral conditions the *o*-hydroxy-substituted phenylethylcarbonate was hydrolysed ten times faster
 3 than the two other compounds. General principles for transcarbonation were given in a very
 4 complete review on carbonates in 1996.²²⁵ Generally, the more nucleophilic alcohol displaces the less
 5 nucleophilic one and in the case of equal nucleophilicity, the less volatile alcohol displaces the more
 6 volatile one. This rule does not apply to phenols, as dialkylcarbonates react with phenols to make
 7 diarylcarbonates. In addition, alcohols bearing bulky groups or electron-withdrawing groups are
 8 poorly reactive. On the contrary, when the carbonate contains electron-withdrawing groups the
 9 alcohol exchange is accelerated. For instance fluorinated dialkylcarbonates and diarylcarbonates
 10 bearing –NO₂, –CN or –Cl groups on the ortho position undergo much faster alcohol exchange (Figure
 11 13b). The activation is less noticeable when the substituents are on the para position. Brunelle et al.
 12 harnessed this effect with the use of a catalyst. Hence, they successfully polymerized
 13 orthonitrophenylcarbonates with bisphenol A at room temperature and even below²²⁶ whereas high
 14 temperatures (up to 200-300 °C) are usually required to prepare polycarbonates.²²⁷ The exchange
 15 between nitrophenylcarbonates and phenol was twice faster with the ortho-substituted carbonate
 16 than with the para-substituted homolog (Figure 13c). Similarly, *bis*-trifluoroethylcarbonates were
 17 shown to exchange with various alcohols and phenols in refluxing heptane or toluene (at 98 and 111
 18 °C respectively) in the presence of a base,^{225,228} and their reactivity was reported to be between the
 19 very reactive dimethylcarbonate and the less reactive diphenylcarbonate (Figure 13d).



20
 21 Figure 13. a. Structures investigated by Tillett and Wiggins²²⁴ b. Effect of electron withdrawing groups (EWG) position on the
 22 exchange rate²²⁵ c. Polymerization rate of nitrophenylcarbonates with bisphenol A depending on the substituent position²²⁶
 23 d. Effect of CF₃ substituent on the exchange rate.²²⁹

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

1 40 minutes were sufficient to reach similar molar masses (Figure 14). This polymerization is
2 composed of two successive substitutions. The rates of the first and second substitutions were
3 reported to be 30-times and 9-times higher for the BMSC-BPA system respectively. Although this
4 study focused on the direct overall two-step reaction, the rate of the reverse reaction for the first
5 substitution was determined for both BMSC and DPC. Indeed, the rate of the first step reverse
6 reaction for DPC was half that of the direct reaction, whereas for BMSC it was three decades lower.
7 The overall two-step reaction is an equilibrium. When this equilibrium was reached for the DPC-BPA
8 system, the main product was the monosubstituted compound, and the same amounts of starting
9 carbonate and disubstituted product were observed. In contrast, for the BMSC-BPA system, the
10 disubstituted carbonate was the main product, the monosubstituted product was also present as
11 byproduct whereas no starting material remained, suggesting that the equilibrium was more
12 displaced toward the products in this case. Such observation is significant for the design of vitrimers
13 based on exchangeable carbonate bonds.



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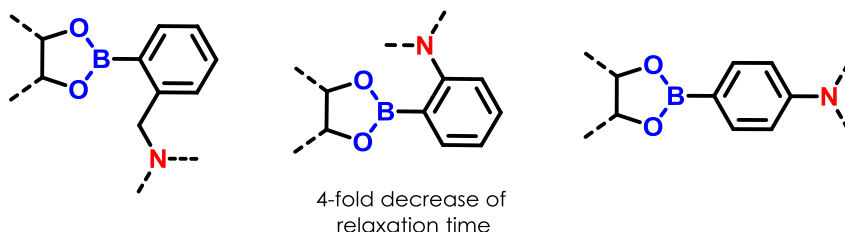
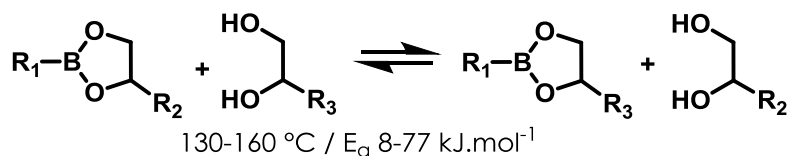
16 *Figure 14. Polymerization of bis-methylsalicylcarbonate (BMSC) and diphenylcarbonate (DPC) with bisphenol A (BPA).²²⁷*

17

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

26

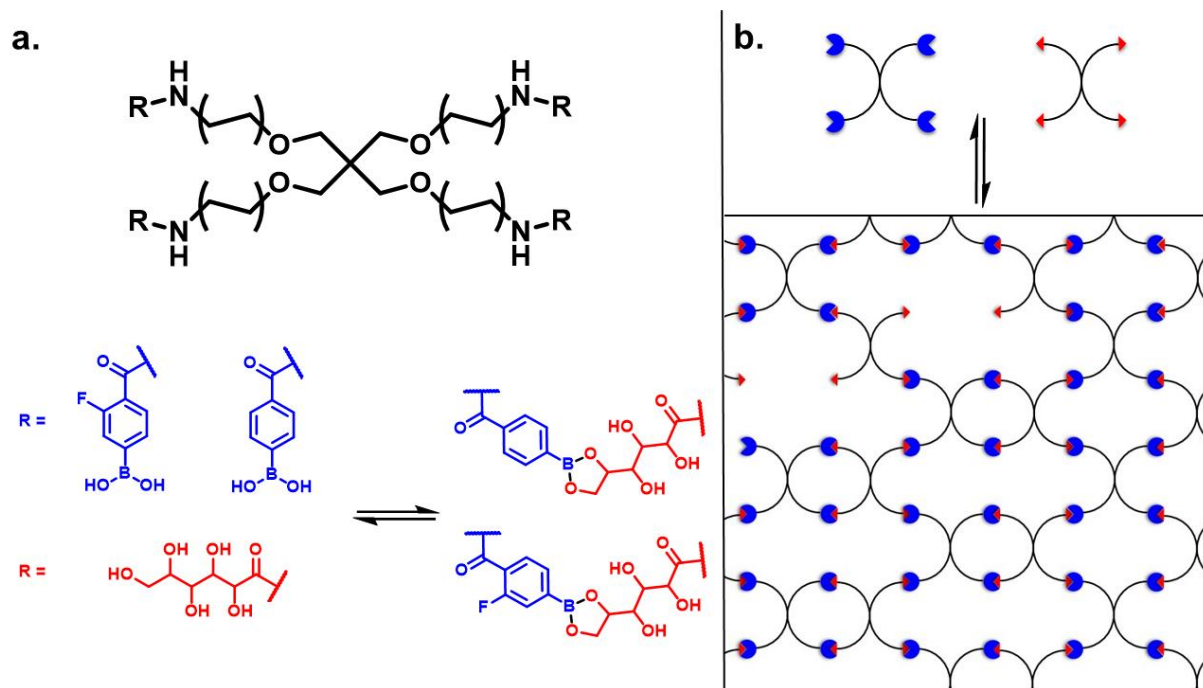
1 Dioxaborolane transesterification acceleration



2

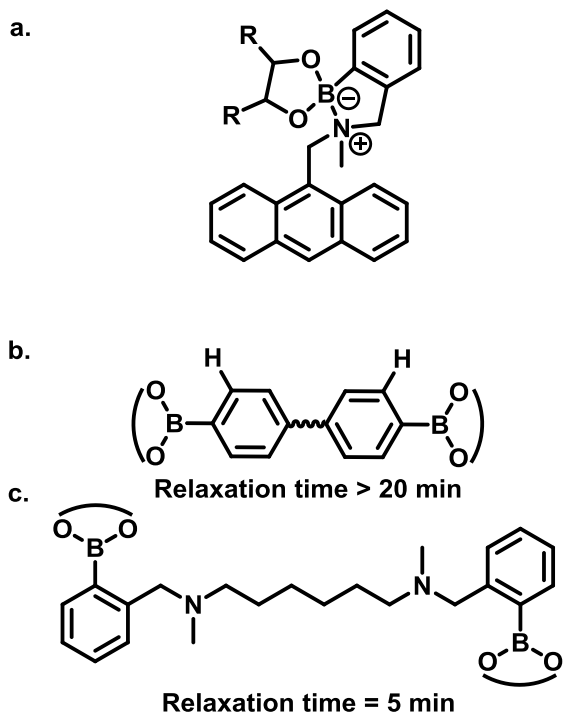
3 *Figure 15. Reported activating groups enhancing dioxaborolanes exchange rate, range of stress-relaxation experiments*
 4 *temperatures²⁵ and activation energies.²⁴*

5 As discussed previously, boronic esters were mainly used in aqueous media. Therefore, the effects of
 6 activating groups on boronic esters were mainly described under such conditions. Although the
 7 behaviour of an exchangeable bond is very different in solution and in the bulk of a material,
 8 especially with a peculiar solvent such as water, it may still be possible to draw general conclusions
 9 on the effects of activating groups (Figure 15). In aqueous solution, there is an equilibrium between
 10 the dissociated boronic acid-diol couple and the corresponding boronic ester. The formation of a
 11 boronic ester by reaction between a boronic acid and a diol must be performed at a pH higher than
 12 the pKa of the acid.^{232,233} Interestingly the pKa of boronic acids can easily be tuned by chemical
 13 modification. For instance, compared to the pKa value of 8.8 of phenylboronic acid, the pKa of
 14 methylboronic acid is 10.4 whereas the pKa of the very electron-withdrawing 3-pyridyl boronic acid is
 15 4.0.⁸⁴ This shift of the esterification equilibrium gives a glimpse of the possible electronic and internal
 16 catalysis effects. An early study showed that arylboronic acids bearing *ortho*-neighboring groups
 17 containing oxygen, sulfur or fluorine do not enhance the esterification nor the transesterification.²³⁴
 18 Nevertheless, electron-withdrawing groups decrease boronic acid pKa whereas electron-donating
 19 groups increase it,^{83,84} and destabilize the ester bond. For instance, the boron atom of phenylboronic
 20 acids are reported to be highly electron deficient, which reduces the pKa and facilitates ester
 21 formation.^{84,233,235} Recently, benzoxaborole-crosslinked polyethylene glycol (PEG) networks were
 22 synthesized out of 4-carboxy-3-fluorophenylboronic acid along with its non-fluorinated counterpart
 23 (Figure 16). Four-arm amine-terminated PEG was modified with 4-carboxy-3-fluorophenylboronic
 24 acid or 4-carboxy-phenylboronic acid to afford tetrafunctional boronic acids. The same procedure
 25 was applied to d-glucolactone to obtain a tetrafunctional diol. Each tetrafunctional acid was then
 26 reacted with the tetrafunctional diol to make a network (Figure 16). This study showed that the
 27 resulting partially fluorinated material had a higher dynamic modulus and a faster relaxation time
 28 than the non-fluorinated analog.²³⁶



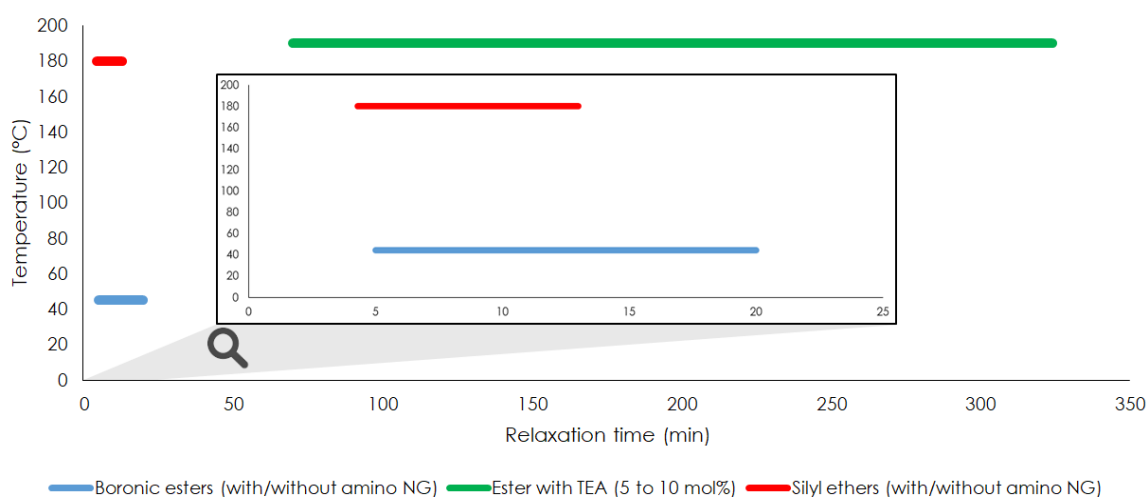
1
 2 *Figure 16. Synthesis of a network based on boronic esters a. polyethylene glycol (PEG) monomers functionalized by boronic*
 3 *acids (blue) and diols (red) and their equilibrium with the boronic ester form b. schematic representation of the network.*²³⁶

4
 5 Nevertheless, the most studied and most promising activating groups so far are nitrogen-containing
 6 groups. Aminomethyl-substituted arylboronic acids were shown to be esterified several orders of
 7 magnitude faster than non-substituted phenylboronic acids.²³⁷ Their transesterification was also
 8 accelerated compared to unsubstituted boronic acids or such acids bearing substituents containing
 9 oxygen, sulfur or fluorine.^{234,238} In solution the addition of a dimethylaminomethyl group on a
 10 phenylboronic ester was shown to accelerate the rate of transesterification by five orders of
 11 magnitude.⁴⁴ Amino group on the ortho or para position decreases the pKa of phenylboronic acid,²³³
 12 and facilitates the formation of ester.²³⁹ This is due to electronic substituent effects on the aromatic
 13 ring. Even when the amino moiety is not directly attached to the aromatic ring, the acceleration
 14 effect is noticeable. In this case, the effect is caused by the formation of B-N dative bonds (a proper
 15 example of neighboring group participation, Figure 17a).^{83,85,233,239}



1
2 Figure 17. a. Example of coordinative B-N bond²³⁹ b. Slow exchange crosslinker and c. fast exchange crosslinker (bottom)
3 studied by Guan et al.⁴⁴

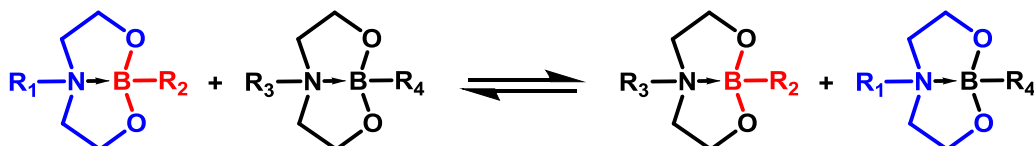
4 Interestingly, amino activating groups have been implemented in vitrimers.⁴⁴ They demonstrated an
5 accelerating effect on boronic esters transesterification in bulk, which enabled the tuning of the
6 properties of dioxaborolane vitrimers. Indeed materials containing amino activating groups relaxed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



9
10 Figure 18. Effect of amine activating groups on the relaxation time of vitrimers with different kinds of exchangeable bonds
11 (NG stands for neighbouring group and TEA for triethanolamine).

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

1 the low mobility of the chains limited the availability of the binding sites.^{87,232} Great care should be
 2 taken in the design of the exchangeable bond as the effect obtained can be opposite to the expected
 3 one in some cases. For instance, in a recent study, vitrimers based on nitrogen-coordinating cyclic
 4 boronic diesters were synthesized, with a dative B→N bond embedded in the cyclic diester (Figure
 5 19).²⁴¹ This particular structure offered an improved resistance to hydrolysis, but also lowered the
 6 exchange rate compared to other cyclic boronic esters. In this particular case the effect on
 7 transesterification is somewhat counterintuitive. In summary, boronic esters in polymers allow the
 8 fine tuning of materials properties thanks to activating groups⁸⁴ with electronic and/or steric effects.
 9 This feature is interesting for vitrimers design. However, the knowledge on these effects in bulk
 10 remains scarce and deserves further investigations.²³⁶

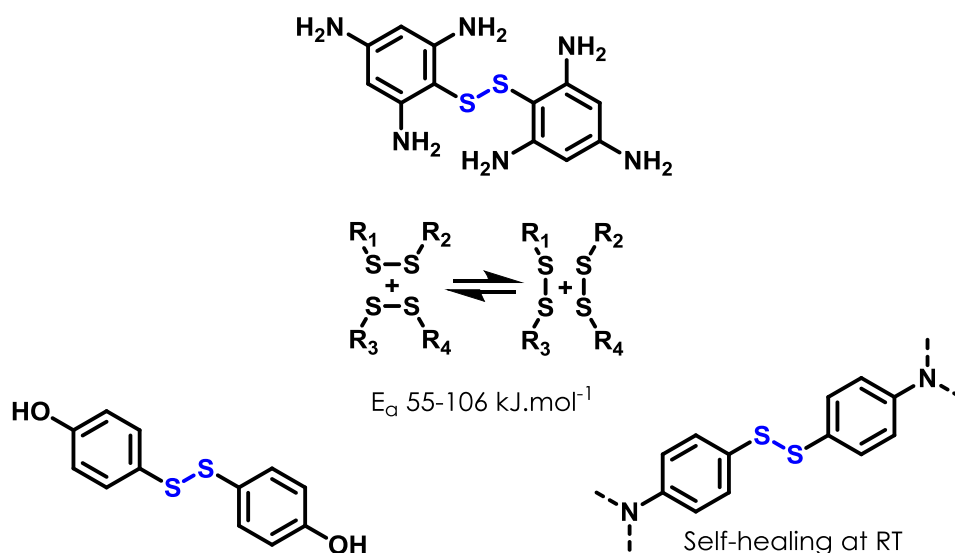


11

12 *Figure 19. Nitrogen-coordinating cyclic boronic diester exchange²⁴¹*

13

14 Disulfides metathesis: effect of aromatic substituents

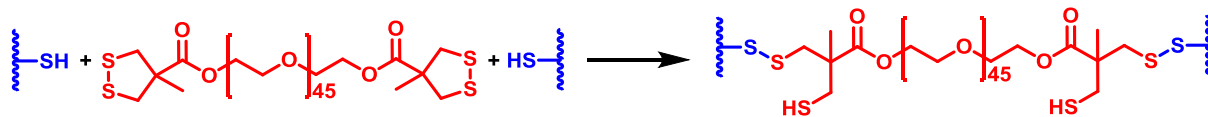


15

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

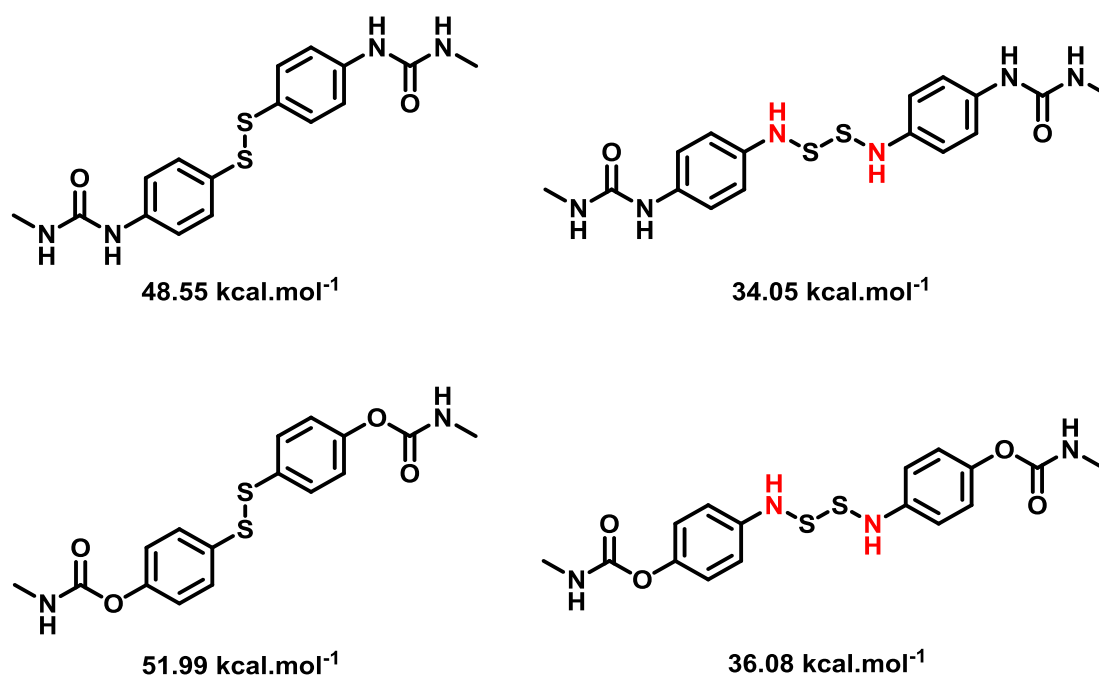
17 Neighboring group participation (NGP) in the exchange of disulfide bonds has hardly been probed
 18 yet, and the data readily available on this topic focus on the dissociative [2+1] radical assisted
 19 mechanism previously discussed in the “Disulfides” paragraph of Part II (Figure 20). However, this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

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



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

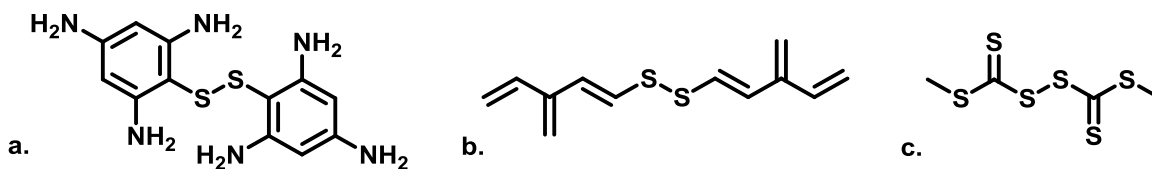
10 Nitrogen has an enhancing effect¹¹⁰ in different kinds of activating groups such as tertiary amines on
 11 phenyl disulfides,^{111,247} thiuram disulfides²⁴⁸ or sulfenamides.²⁴³ For instance aromatic sulfenamide-
 12 derived disulfides (Figure 21) exhibited a bond dissociation energy (BDE) of around 35 kcal.mol⁻¹
 13 whereas their nitrogen-free counterpart exhibited a BDE around 50 kcal.mol⁻¹.²⁴³ The lower is the
 14 BDE, the more radicals are generated, and the easier is the exchange reaction. Thanks to the
 15 enhancement of the exchange reaction, some catalyst-free materials based on aromatic disulfides
 16 exhibited self-healing at room temperature.¹¹⁶ In those materials bis(4-aminophenyl)disulfides were
 17 used as dynamic crosslinkers to make poly(urethane-urea) systems.



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

21 4-hydroxyphenyl disulfides are known to undergo faster radical generation than their 4-aminophenyl
 22 homologs¹¹³ but this effect is still poorly documented. 4-hydroxyphenyl disulfide exchange reaction
 23 with diphenyl disulfide reached 60 % conversion in only 2 h whereas 12 h were necessary for the 4-
 24 aminophenyl disulfide with diphenyl disulfide under UV radiation. Matxain et al. published a
 25 thorough theoretical reactivity study on disulfide bonds dissociation energy.¹¹⁰ They pointed out that
 26 electron donating groups lower the energy of the dissociation and reversely electron withdrawing

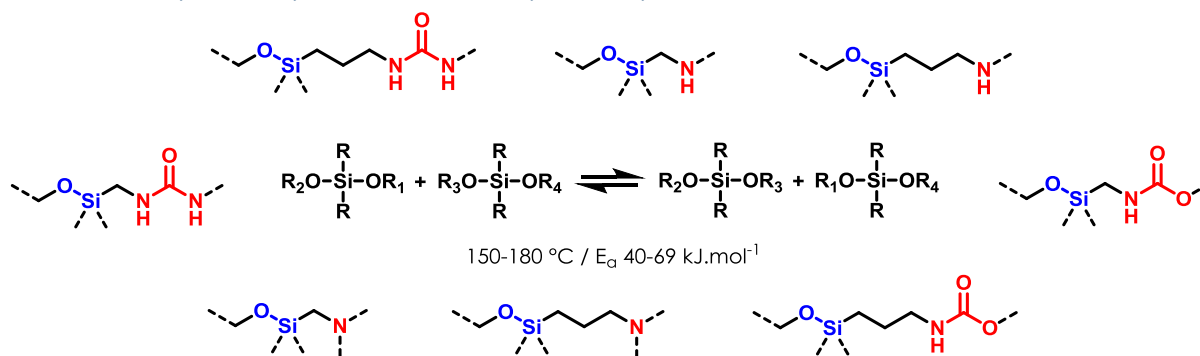
1 groups (EWG) increase it. Compared to the 48 kcal.mol⁻¹ BDE value of unsubstituted aromatic
 2 disulfides, *p*-sulfonic acid substituent increased this value to 55.6 kcal.mol⁻¹ whereas an amino
 3 derivative in *para* position decreased the BDE to 41.3 and even to 30.1 kcal.mol⁻¹ with the
 4 trisubstituted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



10

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

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

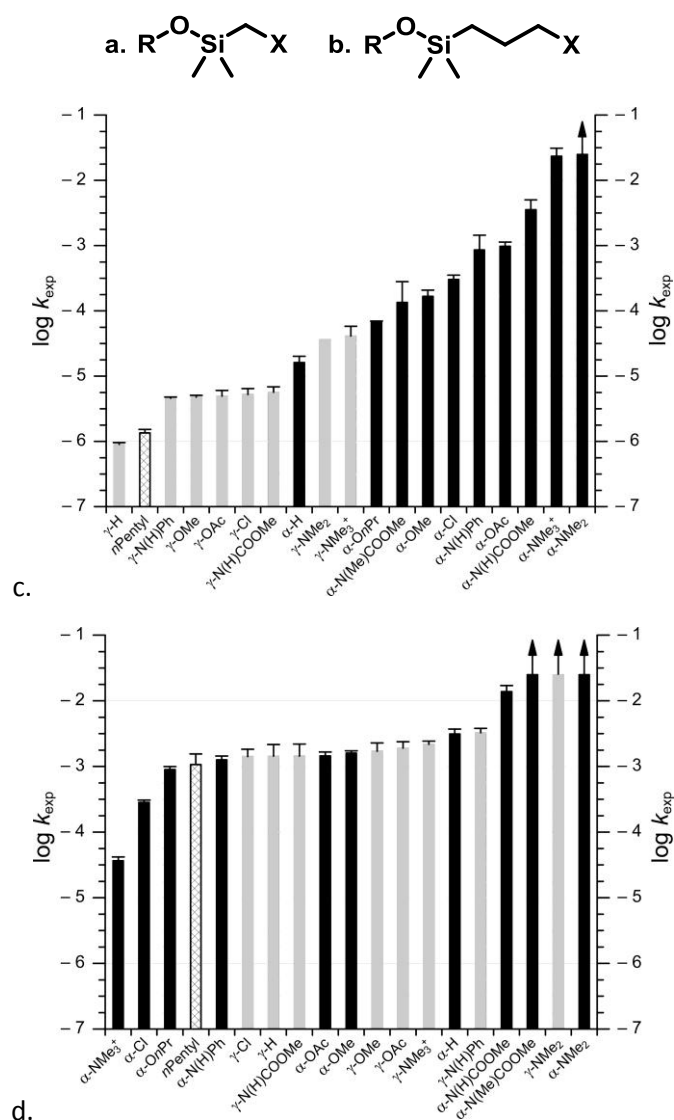


13

14 Figure 23. Examples of activating groups enhancing silyl ether exchange and range of stress-relaxation experiments
 15 temperature²⁵ and activation energies.²⁴

16 When implementing the previously discussed ion pair dissociation-triggered mechanism in silyl
 17 ethers, the main parameters to tune the exchange reactivity are obviously the nature¹³¹ and
 18 concentration¹³⁰ of the ion pairs. The environment of the counterion influences its ability to
 19 dissociate and thus the rate of the exchange reaction (Figure 23). For instance, cation complexation
 20 by oxygen atoms on neighboring siloxane chains was reported to increase the electrophilic behavior
 21 of silicon atoms and the nucleophilic behavior of silanolate moieties, facilitating trans-siloxanation.¹³¹
 22 In 1970, Wright et al. studied the equilibrium between chains and rings in [R(CH₃)SiO]_x structures,
 23 showing that, for x=2 or 4, bulkier R led to favored cyclization. However, the opposite effect was
 24 shown for x>10.²⁴⁹ Catalysis by triphenylphosphine (TPP) and triazabicyclodecene (TBD) in silicone
 25 materials was also reported. TPP led to materials with a temperature of plastic flow around 240 °C
 26 whereas the materials containing TBD flowed at 120 °C.²⁵⁰ In 2014, tertiary and secondary amines,
 27 urea and carbamate groups on α- and γ-silanes (Figure 24) were reported to interact with the alkoxy
 28 leaving group or the attacking nucleophile thus increasing the hydrolysis rate of the alkoxy group.
 29 This study carried out both in solution and *in silico* showed the significant influence of several
 30 activating groups. For instance, secondary amines accelerated the hydrolysis reaction from 5 to 50
 31 times and tertiary amines at least 40 times. Carbamate groups accelerated the reaction from 6 to 80
 32 times, depending on their position and structure.²⁵¹

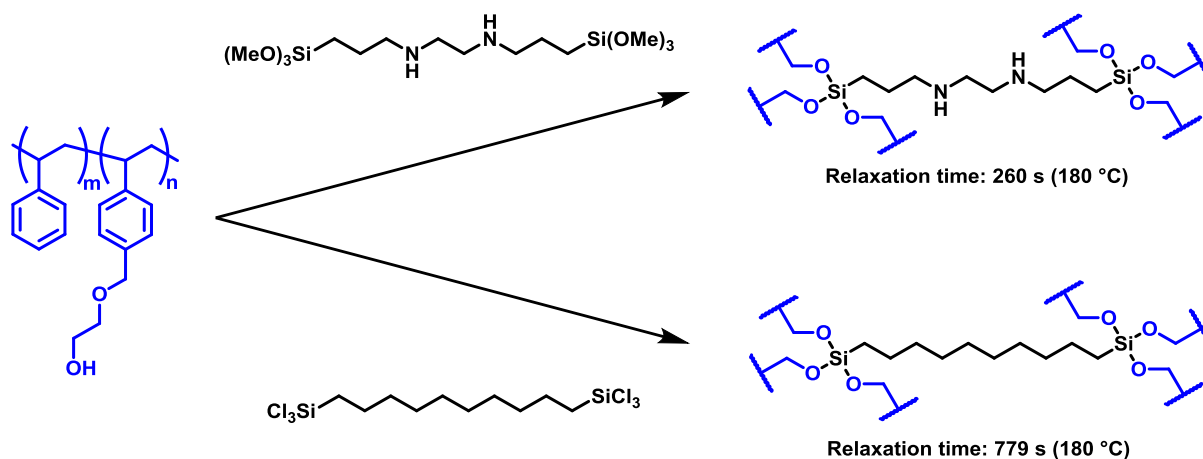
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2

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

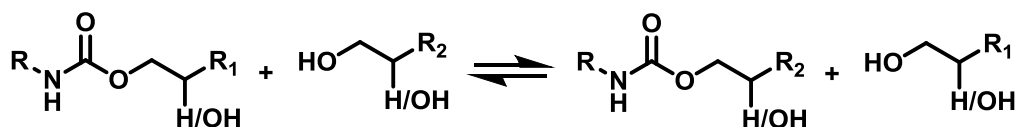
5 This result was later successfully implemented in malleable materials with activating amino moieties
 6 accelerating the exchange rate of silyl ethers.^{45,252} A copolymer of styrene and 2-((4-
 7 vinylbenzyl)oxy)ethan-1-ol was synthesized by free radical copolymerization. Then the resulting
 8 copolymer was crosslinked either with *N,N'*-bis(3-(trimethoxysilyl)propyl)ethane-1,2-diamine or with
 9 1,10-bis(trichlorosilyl)decane (Scheme 30). Both crosslinked structures were similar and the
 10 crosslinkers used had the same length. The relaxation time for the structure incorporating secondary
 11 amines was 260 s at 180 °C, three times less than the 779 s needed for the amine-free structure
 12 (Scheme 30).⁴⁵ Variations of the silyl ether bulkiness and the polymer backbone are suggested to
 13 tune the properties of these materials.¹³²



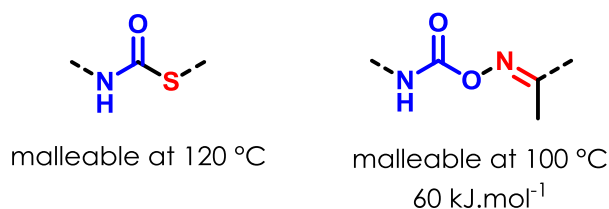
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2

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

5 The case of urethanes and hydroxyurethanes



Stress-relaxation 170-190 °C / E_a PU 114-184 kJ.mol⁻¹ / E_a PHU 99-159 kJ.mol⁻¹



6

7 Figure 25. Characteristics of polyurethanes, polyhydroxyurethanes, polythiourethanes and poly(oxime-urethanes): range of
8 stress-relaxation experiments temperatures²⁵ or reprocessing temperatures and activation energies.^{24,253}

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

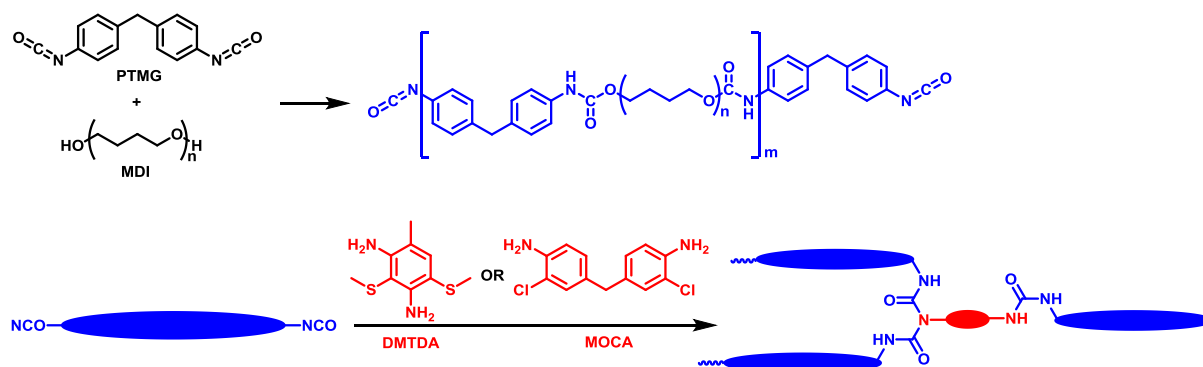
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17 For thiourethanes solvolysis by thiols, secondary amines or alcohols suggested the reaction pathway
18 was an associative addition/elimination mechanism²⁵⁷ instead of the dissociative
19 elimination/addition commonly accepted. Nonetheless, as previously pointed out, the recent
20 implementation of thiourethane bonds in materials highlighted a dual associative and dissociative
21 mechanism.²⁵⁸ Knowledge on the effects of activating groups on hydroxyurethane-based vitrimers is
22 very limited. Nevertheless an excess of free exchanging dangling groups, namely alcohol groups for
23 polyurethanes and thiol groups for polythiourethanes were shown to favour the associative pathway

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

14 Ureas exchange

15 Recently a polyurethane-urea elastomer was claimed to be a vitrimer.²⁵⁹ The authors first
 16 synthesized a PU prepolymer out of poly(oxatetramethylene) glycol (PTMG) and 4,4'-
 17 diphenylmethane diisocyanate (MDI). Then this prepolymer was mixed either with 3,5-dimethylthio-
 18 2,4-toluenediamine (DMTDA) or with 3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA) to form
 19 exchangeable biuret groups (*N,N'*-diaryl urea) (Scheme 31). Because the diamines used are primary,
 20 each amine is able to react twice thus ensuring the formation of a crosslinked materials (primary
 21 diamines can be considered as hidden tetrafunctional reactants). The amines used bore either
 22 electron-donating methylthio substituents or electron-withdrawing chlorine atoms. The stress
 23 relaxation time of the methylthio groups-containing network was 3 to 4 times shorter than that of
 24 the chlorinated analog, depending on the temperature (100 to 120 °C). The relaxation was assigned
 25 to urea-urea exchanges and the mechanism was reported as associative.²⁵⁹ Nevertheless there are
 26 little proofs to support this claim.

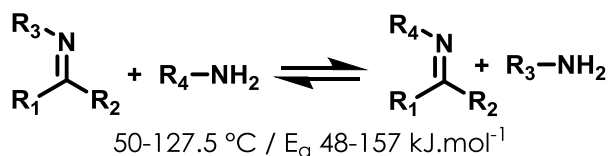


27

28 *Scheme 31. Synthesis of polyurethane-urea self-healable elastomers.*²⁵⁹

29

1 Transimination acceleration by activating groups



2

3 Figure 26. Characteristics of transimination: reported range of stress-relaxation experiments temperatures²⁵ and activation
4 energies.²⁶⁰ Two examples of potentially active neighboring groups are given.

5 The success of imines-derived vitrimers (Figure 26) may be explained by the versatility of this linkage,
6 but also because these vitrimers can be reprocessed without the need for a catalyst.¹⁶³⁻¹⁷⁴ When used
7 in organic chemistry or biochemistry, transimination was reported to be catalysed by thiourea metal
8 complexes (2 orders of magnitude rate acceleration),¹⁷⁷ triflate salts of scandium, terbium, samarium
9 and other lanthanides (up to 5 orders of magnitude acceleration),^{178,261} zinc bromide,²⁶² iron chloride,
10 copper chloride and magnesium chloride.²⁶³ Besides, acid and basic catalysis are known to be
11 efficient as well, in aqueous^{175,264} or organic solutions.^{175,265} In particular, interesting examples of
12 internal basic catalysis in solution were reported in the 1980s, using primary amines featuring an
13 internal tertiary amine function.^{264,265} Ciaccia et al.¹⁸⁰ reported a study on aromatic imines in organic
14 solvents at room temperature. Part of this work dealt with the exchange between *N*-
15 benzylideneanilines and *p*-toluidine (Figure 27). The exchange reaction exhibited low equilibrium
16 constants ($K_{eq} < 10$), thus the results could have been carefully extrapolated to degenerate system
17 such as those encountered in vitrimers. **The** authors showed that the rate of the forward
18 transimination reaction was almost unaffected by EWG and EDG on the imine aromatic ring, but that
19 the reverse reaction was mildly affected by these substituents. Electron-donating $-\text{OCH}_3$ group
20 slightly increased the reverse reaction rate, whereas electron-withdrawing $-\text{CN}$ and $-\text{NO}_2$ groups
21 decreased this rate (Figure 27). Similarly, Schaufelberger et al.²⁶² studied the impact of substituents
22 on the exchange of aromatic imines with benzyl amines in the presence of zinc bromide as catalyst in
23 acetonitrile. Nevertheless, in this system, two simultaneous reactions were involved, imine
24 isomerization and transimination. Thus, it would be dubious to draw general conclusions on internal
25 catalysis based on this study.

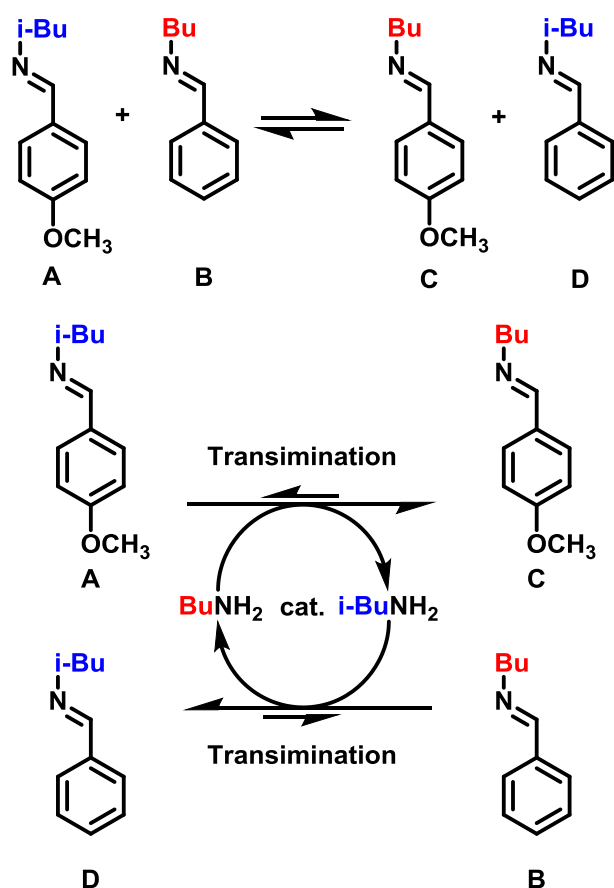
	X	K	k_d ($\text{M}^{-1}\text{s}^{-1}$)	k_r ($\text{M}^{-1}\text{s}^{-1}$)
H	2.6	1.0×10^{-1}	3.8×10^{-2}	
OCH_3	3.0	1.2×10^{-1}	4.0×10^{-2}	
CN	4.5	1.1×10^{-1}	2.4×10^{-2}	
NO_2	7.2	0.94×10^{-1}	1.3×10^{-2}	

26

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

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

1 faster imine exchange than toluene.²⁶⁶ Additionally imine metathesis is catalysed by zirconium,
 2 molybdenum, rhenium and niobium in organic solvents if the temperature reaches 100 °C¹⁷⁹ and by
 3 hafnium imido complexes at 80 °C as well.²⁶⁷ An interesting strategy involving minute amounts of
 4 primary amines was also reported to accelerate this reaction in solution at room temperature.¹⁷⁹ The
 5 effect of primary amines on imine metathesis was investigated in terms of mechanism and
 6 thermodynamics. Mechanistically speaking the overall reaction can be seen as two concomitant
 7 transimination reactions (Scheme 32). Thus, it is not *stricto sensu* an imine metathesis, but the
 8 overall result is the same. Minute amounts of an imine A bearing an isobutyl group exchange with
 9 the minute amount of n-butylamine leading to the release of minute amounts of the exchanged
 10 imine C and isobutylamine. This amine then undergoes transimination with an imine B bearing a n-
 11 butyl group. This second step releases the exchanged imine D and n-butylamine able to react with A,
 12 and so on. The overall reaction is an equilibrium between amines A and B on one hand, C and D on
 13 the other. Thermodynamically speaking the overall reaction is an imine metathesis.¹⁷⁹ This effect was
 14 implemented in imine-crosslinked PEG networks. A slight excess of dangling primary amines enabled
 15 self-healing at 50 °C within 5 min.²⁶⁶ Thus choosing carefully the stoichiometry for the synthesis of
 16 imine-derived vitrimers would enable the tuning of their properties.



17

18 *Scheme 32. Imine metathesis catalysis by minute amounts of primary amines.*¹⁷⁹

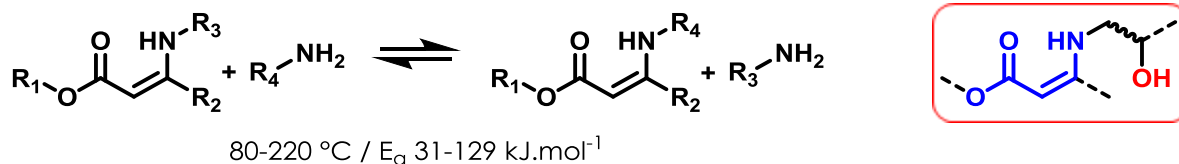
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20 Recently the effect of hydrogen bonds was also emphasized. Indeed hydrogen bond donors such as
 21 thioureas and squaramides catalysed both imine metathesis and transimination in solution and their
 22 efficiencies depended on their structures.²⁶⁸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

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

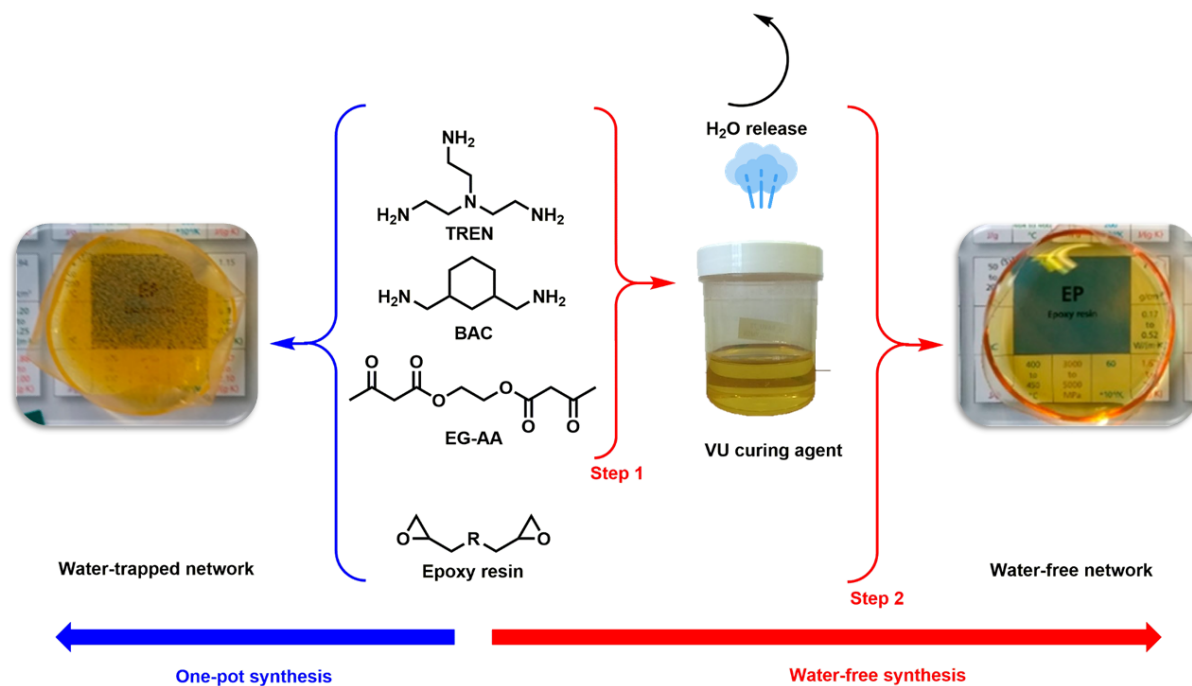
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4 Vinylogous urethanes and amides, an efficient exchange chemistry without catalyst



6 *Scheme 33. Characteristics of vinylogous urethane transamination: reported range of stress-relaxation experiments*
7 *temperatures²⁵ and activation energies.²⁴ Dangling hydroxyl groups accelerates the relaxation time of VU materials.*

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



1

One-pot synthesis

Water-free synthesis

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

6 Hints for diketoenamines activation

7 As previously mentioned, diketoenamines were essentially studied as protecting groups and there is
 8 no extensive knowledge on a potential effect of neighboring groups. Nevertheless, in the work of
 9 Augustyns et al.²⁰¹ already discussed earlier, a few interesting trends on reactivity were gathered.
 10 The two amino groups on lysine did not have the same reactivity toward the exchange of Dde group.
 11 Unprotected ϵ -NH₂ groups could exchange with protected ϵ -NH₂ and α -NH₂ groups but free α -NH₂
 12 groups could not exchange Dde with ϵ -NH₂. This was probably because α -NH₂ groups were too
 13 sterically hindered and not nucleophilic enough due to the neighboring electron-withdrawing
 14 carboxylic acid. In addition, when 2-acetyldimmedone was reacted with polyamine, primary amines
 15 were selectively protected.²⁰¹ The use of diketoenamines in vitrimers is just starting to emerge and
 16 there is undoubtedly a lot to discover on this chemistry, based on the encouraging proof of concept
 17 recently disclosed.^{204,205}

18 Effect of the alkylating agent on trialkylsulfonium salts exchange

19 As mentioned before, the knowledge on trialkylsulfonium exchange with thioethers is poor except
 20 for the proof-of-concept disclosed by Du Prez's group.⁴⁰ Of course, the most obvious parameters to
 21 tune the material reprocessability are the nature and quantity of the alkylating agent. Without
 22 alkylating agent, no stress relaxation was observed in polythioether.⁴⁰ Conversely increasing the
 23 concentration of the butyl brosylate alkylating agent from 1 to 10 mol% decreased relaxation time at
 24 150 °C from 75 to 10 mins.⁴⁰ The same behaviour was observed using trimethylsulfonium iodide as
 25 alkylating agent.¹²⁴ Once again, there might be room for internal catalysis studies with this kind of
 26 chemistry. Indeed, this exchange reaction was studied on small arylalkylsulfides in solution. If no
 27 change in the kinetics was observed with electron-rich aromatic groups, electron-poor aromatic
 28 groups slowed down the conversion rate. The alkyl substituent bulkiness also played a role.
 29 Phenylalkyl sulfides bearing various alkyl groups were transalkylated with methyl iodide. *Tert*-butyl-
 30 phenyl sulfides reached full conversion in 25 hours whereas the butyl-, 3-pentyl- and 2,2-

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

6

1 Conclusion and outlook

2

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

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