SCIENTIFIC PERSPECTIVE

A Highly Dynamic Covalent Polymer Network without Creep: Mission Impossible?

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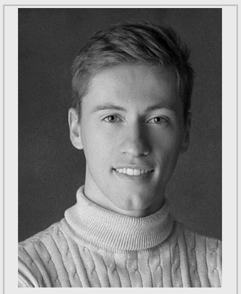
Abstract: Dynamic covalent polymer networks provide an interesting solution to the challenging recyclability of thermosets and elastomers. One of the remaining design constraints, however, is balancing thermal reprocessability in the form of material flow with dimensional stability during use. As a result, many chemistries are being investigated in order to improve bond reactivity control and material robustness. This Minireview highlights a number of promising concepts, with a particular emphasis on disconnecting chemical reactivity in low and high temperature regimes to obtain creep resistant, yet highly dynamic polymer networks. In addition, we will highlight the impact of sharp reactivity changes when applying extrapolation-based approaches during rheological analysis. As a result, we are confident that abandoning the myth of 'permanent' reactivity will aid in the development of sustainable polymeric materials that can truly combine the benefits of thermoplastic and thermoset behaviour.

1. Introduction

Plastic pollution has quickly become one of modern society's most pressing environmental issues.[1,2] While there are many facets to this global challenge,[3] thermomechanical recycling of polymer waste is the most commonly used strategy for transitioning from discarded products to resources.[4,5] For this, heat and mechanical mixing are sufficient to break the interactions between polymer chains and initiate material flow. While this plastic (re)processing faces its own set of technical hurdles, such as contamination and thermal degradation,[4,6] much progress is still being made as a result of important drivers such as legislation and market demand. This approach, however, is not applicable to thermosets, or any type of covalently cross-linked polymer structure, because they do not allow for flow upon heating but rather decompose due to a much stronger bonding between chains.[7] In fact, thermoset molecular architectures are explicitly designed to withstand the influence of mechanical stress and heat to resist unwanted deformation or creep. Therefore, thermosets make up some of the most durable polymer materials, but at the same time they are inaccessible as a resource once made.

Filip *Van Lijsebetten* In 2019, he received his Master's degree in Chemistry from Ghent University (Belgium), where he worked on his thesis on sequence-defined macromolecules. He was awarded a Ph.D. scholarship from the Research Foundation Flanders (FWO) in October 2019 to work on the development of industrially applicable dynamic polymer networks. One of his main goals is to address (re)processability and recyclability issues for cross-linked materials.



Dr. Tapas Debsharma received his Ph.D. in polymer chemistry in 2019 from the University of Potsdam with the thesis entitled “Cellulose derived polymers: synthesis of functional and degradable polymers from cellulose”. Since 2020, he is a postdoctoral researcher at Ghent University in the group of Prof. Dr. Filip Du Prez, dealing with recyclable thermoset materials and their applications in composites.

Prof. Dr. Johan Winne Since 2015, he has been the group leader of an organic synthesis group that shares his fascination for the chemistry of natural products, heterocycles, and cycloadditions. Apart from tackling fundamental problems in organic reactivity and explorative reaction design, he developed an interest in responsive systems through joint projects with Filip Du Prez in the development of novel materials based on dynamic covalent chemistries.

Prof. Dr. Filip Du Prez Since 1999, he has led the Polymer Chemistry Research Group (www.PCR.UGent.be) at Ghent University's Centre of Macromolecular Chemistry (CMaC), which includes about 25 researchers working on the design of dynamic/renewable polymer materials as well as the development/application of novel polymer structures such as sequence-defined polymers. He has been an associate editor of Polymer Chemistry since 2018, and in 2021, he was awarded an ERC Advanced Grant for his work on circular thermoset materials.

Moving away from the traditional distinctions between (thermo)plastics and thermosets, recent research has shown that material flow can still be introduced into cross-linked materials *via* so-called dynamic covalent bonds.[8–16] More specifically, polymer chains can rearrange themselves by using bonds that are exchangeable or reversible in response to a specific trigger (mostly heat). As a result, a dynamic covalent network, often referred to as a covalent adaptable network, is formed that can behave like classical thermosets under defined conditions, while also being reprocessable like a thermoplastic, following the activation of a chemical reaction. However, for true industrial application, bond exchange should be highly activated and very fast during processing at elevated temperatures that can avoid degradation of organic material (>200-250 °C), but at the same time are sufficiently slow and deactivated during ‘normal’ use to sufficiently suppress creep.[17,18] This is a difficult task that has in fact been recognised since the first reports on dynamic covalent chemistry in polymer networks in the 1940s and 1960s.[19–21] A thorough understanding of how and to what extent chemical reactions can be activated and controlled within a polymer network is therefore critical.

In this Minireview, we aim to focus on the key physical and chemical factors that are known to control when and to what extent a dynamic covalent network exhibits plastic behaviour such as flow or creep. Before outlining the various examples of creative solutions to the fundamental creep problem that have been reported to date, an overview of how molecular behaviour of cross-links can be related to macroscopic material properties is provided. Monitoring chemical reactivity within an inherently insoluble polymer network is not a trivial task, and observed small molecule reactivity will mostly not translate well to such a matrix, as important quantitative and qualitative differences can be expected and have been observed. Therefore, the best practices, advantages, and disadvantages of characterising both long-term and short-term chemical reactivity are discussed.

2. Characterising the onset of material flow

To practically determine the onset of material flow, temperature-dependent behaviour of polymers is frequently determined by their mechanical response to deformation or rheology.[22,23] During linear rheology experiments, viscoelastic regions are defined based on temperature-induced changes in physical behaviour. The link between these regions provides a distinct *viscosity shift* that can span a wide range of temperatures.[24–26] The region of interest for dynamic covalent networks is the rubbery phase where bond rearrangement occurs without taking diffusion constraints into account. Indeed, because of the slow segmental motion associated with the glass transition, dynamic covalent

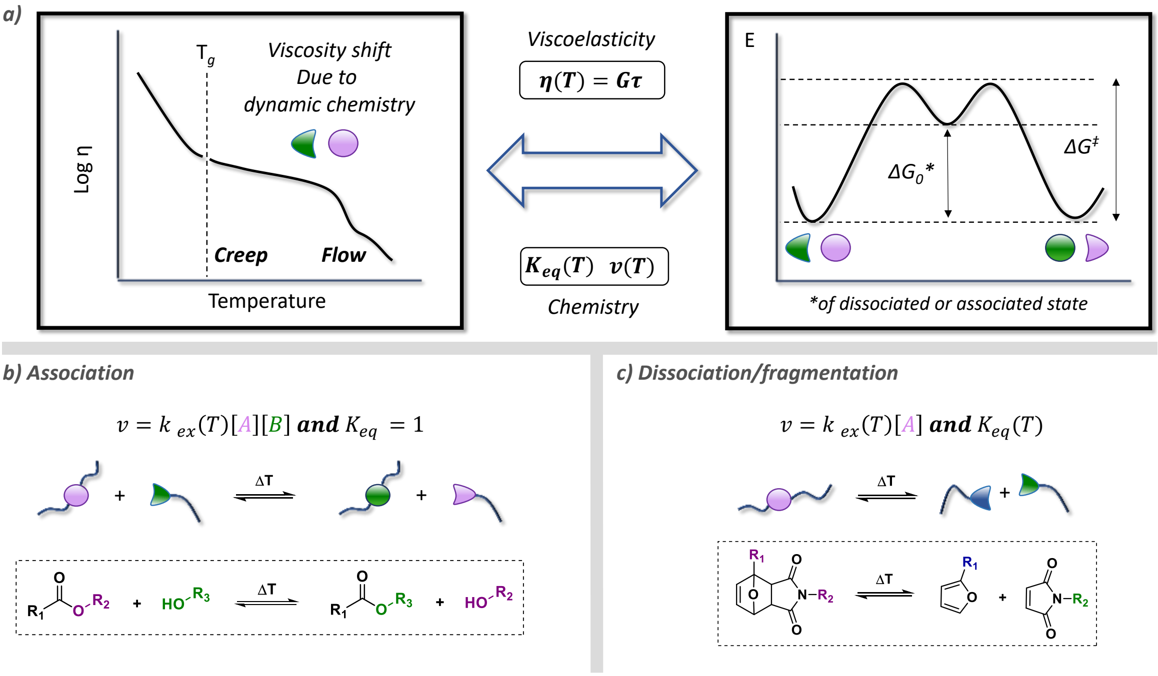


Figure 1. a) Temperature-dependent chemical reactivity controls the macroscopic properties of dynamic covalent polymer networks, resulting in a unique dynamic covalent viscosity shift. b) Bond exchange requires prior association of polymer chains (e.g. transesterification).[9] c) Bond dissociation results in fragmentation or depolymerisation of polymer chains (e.g. retro Diels-Alder).[11]

chemistry is generally considered to be irrelevant below a material's T_g (*vide infra*).[27–29] Nonetheless, given the increasing number of reports on mechanochemistry and solid state reactions,[30,31] we anticipate that fast chemical reactions will continue to be relevant below a material's T_g, albeit with a greater reliance on external forces to overcome diffusion limitations.

To avoid the need to measure rheology over a very wide temperature range and thus to avoid excessive measurement times, dynamic behaviour at high temperatures and for short periods of time is frequently extrapolated to that at lower temperatures, assuming that the viscosity responds in the same (linear) way. However, due to the interference of, for example, a complex rubber-to-glass transition, this can become quite misleading, even for regular polymer materials that are expected to be chemically inert.[32] While chemical reactivity should not exhibit distinct (phase) transitions, the kinetics and thermodynamics of a chemical reaction are in fact temperature dependent and their thermal response will determine the dominant reaction mechanism(s) underlying a viscosity decrease (**Figure 1a**).[33–37] More specifically, in the ideal case, it should be experimentally validated whether, to what extent and at what rate bond *exchange* or *dissociation* will occur within a given network. An important distinction here, which has been identified before, relates to the fact whether bond rearrangement requires the prior association of two polymer chains ('bimolecular reaction', **Figure 1b**) or if a polymer chain can fragment by itself ('unimolecular reaction', typically followed by a faster non-rate determining recombination of reactive ends, **Figure 1c**). The accurate prediction of the effect of molecular-level reaction parameters on macroscopic properties (its 'dynamic covalent shift') will thus be highly dependent on the experiment and subsequent interpretation over a wide temperature range.[23,34,37–41]

According to the Maxwell relation ($\eta = \tau G$), both the relaxation dynamics ($\sim\tau$) and effective cross-linking densities ($\sim G$) will have an effect on the flow capacity of a dynamic network, which can vary depending on the *kinetics* (v) and *thermodynamic equilibrium* (K_{eq}) of the chemistry involved.[25,38,42,43] Starting from this fundamental relationship, a plethora of reversible reactions and synthesis methods have been reported and are summarised in several comprehensive reviews on this subject.[26,44–46] Additionally, since the introduction of vitrimers, much emphasis has been placed on distinguishing between dynamic covalent networks with underlying associative (*i.e.* vitrimers) or dissociative chemistries. However, because macroscopic reactivity is affected by a variety of other factors, it is always best practice to characterise and rationalise changes in both relaxation rate and cross-linking density with temperature without overly favouring a putative mechanistic type that may or may not be dominant within a dynamic network.[25,33]

For the characterisation of relatively fast dynamic behaviour, stress-relaxation [G(t)] and frequency sweep experiments [G*(ω)] within the linear viscoelastic regime have undeniably been the method of choice. Nonetheless, due to practical limitations, both tests fail to capture long-term processes, which can be more accurately described by linear creep experiments.[47–49] The rate of deformation or creep rate can indeed be used to determine (infinitesimally) slow viscosity changes with temperature.[18,50] Surprisingly, the systematic use of creep measurements to determine whether premature activation of bond rearrangement would significantly harm the applicability of dynamic covalent networks has remained limited in recent literature. This could be ascribed to the fact that the analysis of creep measurements and the resulting parameters are often not (well) known. Nevertheless, an increasing amount of studies on dynamic covalent networks now focus on the development of (potentially) creep resistant behaviour. The most promising examples and strategies are highlighted in the next section. For conciseness, and in order to maintain the focus of this Minireview on chemical strategies, the use of physical fillers is not included in this overview.

3. Controlling material flow

In 2017, Montarnal and co-workers highlighted the importance of designing dynamic covalent materials capable of balancing low viscosities during (re)processing and very high viscosities during use.[17] In other words, above a temperature threshold, a rapid decrease in viscosity is wanted, corresponding to a high apparent *viscous flow* activation energy ($E_{a,flow}$).[25] Keeping the Maxwell relation in mind, it is important to remember that both relaxation (*kinetics)* and cross-linking density changes (shift in *thermodynamic equilibrium)* can contribute significantly to viscous flow. Furthermore, both contributions are temperature dependent,[33] whereby a large shift in reaction rate or equilibrium can cause a deviation from a linear (*i.e.* Arrhenian) viscosity decrease. In fact, for many processing applications a non-linear decrease in viscosity is desirable. Even more so, controlled deviations from 'linear Arrhenius behaviour' over a large temperature range should aid in the development of creep resistant materials.

To obtain drastic changes in viscous flow behaviour, a common design complication is that many solutions that prevent excessive creep involve a reduction in chemical reactivity, which eventually has a negative impact on the material's (re)processability or mechanical properties. In this Minireview article, we will mainly focus on some of the recent chemical design strategies that can be used to induce creep resistance with a specific focus on those that show the potential to combine it with optimal (re)processability, so that the reader can form an opinion on the question in this Minireview's title. For clarity, we have subdivided the main developments in four different sections, which are discussed in a thematic rather than in a chronological order, depending on the key concepts underlying the creep reduction ambitions. As a result, we first summarised the classical factors known to affect the course, rate, and direction of chemical reactions that exhibit the potential for 'thermoselectivity' and become relevant only during reprocessing, which will be discussed in greater detail in the following subsections.

Catalysts

First, we will focus on latent catalysis, whereby a compound or complex will show little to no activity during use temperatures and

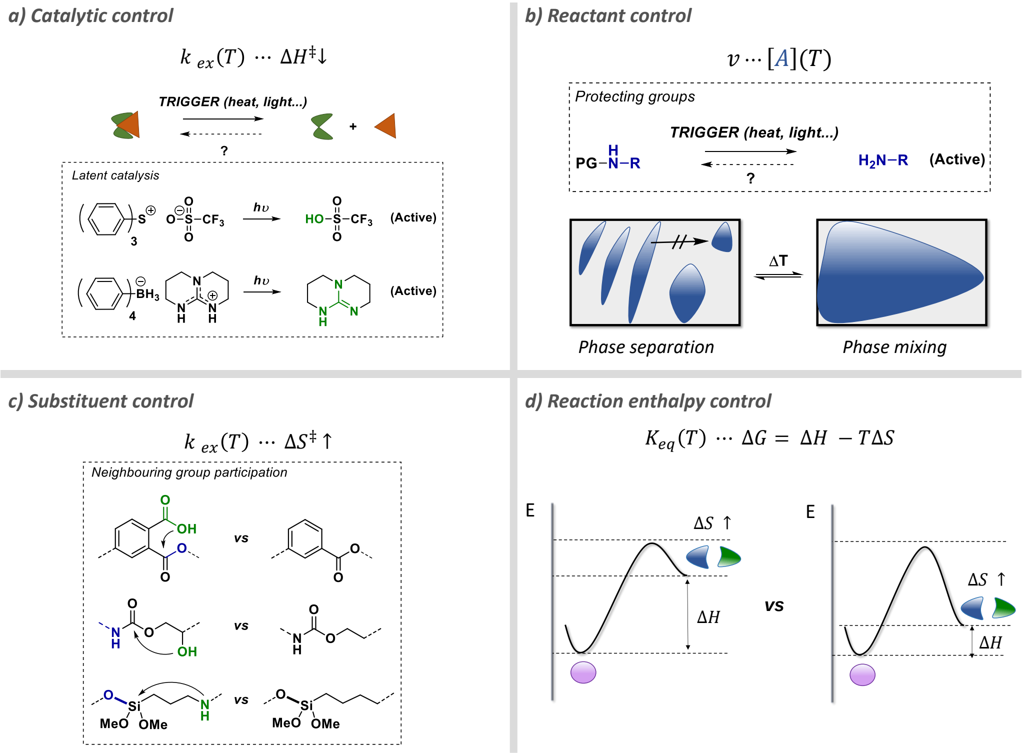


Figure 2. Schematic overview of chemical design strategies that have been applied to enhance creep resistance and retain optimal (re)processability: a) Latent catalysis to control the barrier for reaction; b) Protecting groups and phase separation to control the availability of reactive groups; c) Use of substituents that have a rate-enhancing/inhibiting effect upon activation; d) Use of dynamic covalent bonds that are characterised by a high reaction enthalpy.

initiate only upon activation by a stimulus such as e.g. heat or light (**Figure 2a**). While this is a well-known strategy in polymer science to control the rate and onset of polymerisation,[51] it has remained relatively underexplored in dynamic covalent network research. Nonetheless, using only a small amount of such additives could drastically alter thermomechanical properties if the (de)activated catalyst system is able to avoid premature activation during use.[52–54]

Reactants

For bond exchange, or on a macroscopic level stress-relaxation, to occur, thermal motion should be able to bring reactive species into contact.[55,56] Taking inspiration from multistep organic synthesis, the use of (dynamic) protecting groups and phase separation allows to control the availability of reactants (**Figure 2b**). More specifically, by temporarily masking or avoiding the diffusion of functional groups, reactions are severely limited. Subsequently, when unmasking and phase mixing are promoted upon heating, reactions are activated again.

Substituents

Driven by the need to switch between active and inactive network rearrangement, without the need for (highly reactive) additives, recent literature has focused on 'catalyst-free' dynamic systems that make use of functional monomers that show a rate-enhancing/inhibiting effect upon activation.[57–59] More specifically, reversible heat-promoted participation or light-promoted inhibition of a neighbouring functional group close to a reactive cross-link allows to control the onset of dynamic behaviour (**Figure 2c**).

Reaction enthalpy

A final, but often underestimated strategy for dissociative dynamic covalent networks is to select bonds with a high reaction enthalpy (**Figure 2d**). As such, the generation of reactive intermediates, necessary for dynamic bond exchange, will only occur at higher temperatures when the available thermal energy is sufficient to shift the equilibrium to the entropically more favoured debonded state.[33,60]

3.1. Catalytic control: catalyst loading and catalytic activity

One straightforward approach to control the rate of material flow is to use specific additives or catalysts that can inhibit or accelerate dynamic behaviour.[61–65] In their seminal work, Leibler and co-workers demonstrated that changing the content and nature of the catalyst results in drastic differences in viscoelastic behaviour.[28] For instance, switching from 5 mol% zinc acetate to 5 mol% triphenylphosphine in a polyester-based vitrimer resulted in a reduction in permanent deformation at 200 °C from 35% to below 1%. Changing catalysts or additives can obviously also change the $E_{a,flow}$, and thus thermal response of the reactivity. However, simply decreasing catalyst loading to resist creep will inevitably also impair (re)processability.

To address the disadvantage of 'permanent' catalyst activity, one elegant solution has been to design catalysts that are only available once activated. For example, a thermoset material can be converted to a dynamic covalent network, only after being exposed to light *via* the use of a latent, photo-active base or acid. Bowman and co-workers reported such a method based on the need for a base catalyst for thiol-thioester reactions (**Figure 3a**).[54,66] Before irradiation, in the absence of a base, the thiol-

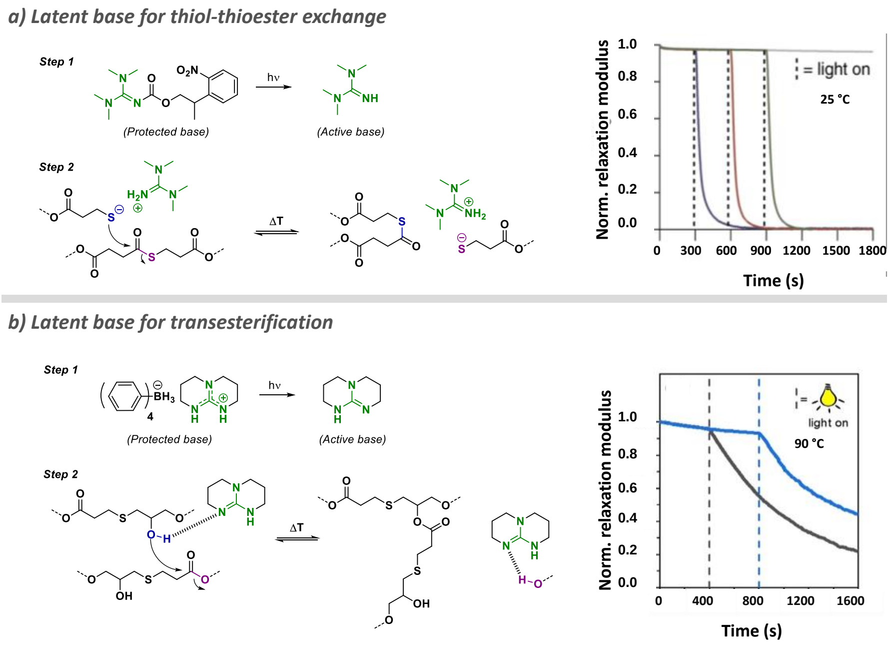


Figure 3. Influence of controlled catalysis on viscoelastic properties of dynamic covalent networks. a) Stress-relaxation at 25 °C indicating the effect of a photo-latent base on thiol-thioester exchange.[54] (Adapted from ref. 55 with permission from Nature research, copyright 2018) b) Stress-relaxation at 90 °C highlighting the drastic increase in transesterification rates by using a UV-deprotectable base.[53] (Adapted from ref. 54 with permission from John Wiley & Sons, copyright 2021)

thioester exchange is characterised by a high activation enthalpy around 150 kJ.mol^{-1}. Upon UV-irradiation, a strong base is released resulting in a drastic decrease of the enthalpic barrier to only 25 kJ.mol^{-1}, promoting rapid flow at room temperature as confirmed by stress-relaxation experiments. While no creep experiments were performed for this specific material, one can envision that fast and permanent switching between an inert and active state by using a UV-deprotectable base is a promising approach to control catalytic activity. Schlögl and colleagues recently extended the concept of photo-latent bases to dynamic polyester networks (**Figure 3b**).[53,67] Non-exposed samples showed no significant relaxation at 90 °C, whereas UV-irradiation resulted in the release of a strong guanidine base and full relaxation in 30 min. In this study, the dynamic behaviour at lower temperatures was extrapolated from high temperature stress-relaxation measurements, which did not allow to determine its long-time flow.

The fact that a specific amount of catalyst can be added or activated during the recycling process makes it an appealing design strategy.[68] Moreover, targeted irradiation allows to precisely and spatially control the shape of the polymer network. On the other hand, after addition or activation, a highly active catalyst is present, which inevitably leads to recycled products with decreased dimensional stability. Nonetheless, it can be expected that the use of additives (with temporary reactivity) will continue to be an important and powerful tool for achieving full control of on-demand viscoelastic behaviour.

3.2. Controlling the availability of reactive functional groups

An obvious factor to control the rate and extent of material flow is to adjust the availability of a reactive chain-end, cross-link or network defect (*i.e.* any molecular chain segment associated in the bond exchange process). For instance, Leibler and co-workers described a simple method for quenching exchange in which the required reactive amine functional groups were chemically blocked with a capping agent after (re)processing, limiting their availability for exchange reactions (**Figure 4a**).[69] More specifically, by reacting the necessary pendent primary amines with a monofunctional acetoacetate, transamination in vinylogous urethane networks could be decreased by a factor of 10 at 100 °C. Although conceptually interesting, the blocking step is practically irreversible, and dynamic behaviour cannot be recovered at higher temperatures. Another more general strategy, reported independently by Sumerlin and Torkelson and co-workers, relied on the partial quenching of polyol/polyester vitrimer reactivity by the substitution of a fraction of dynamic covalent cross-links for permanently cross-linked ones (**Figure 4b**).[70–72] Importantly, for e.g. an epoxy-based polymer network, the authors highlighted that diluting the dynamic part resulted in better performance up to a critical 40 mol% of permanent bonds. More specifically, when comparing a material with only dynamic crosslinks to one with 40% permanent bonds, a slight decrease in relaxation from 1950 s to 2500 s at 160 °C resulted in a 71% reduction in creep at 150 °C for 48 h. However, when further increasing the content of permanent bonds, an accumulation of residual stress leads to a loss in property recovery after thermal cycling.[72,73] Although creep measurements were solely reported at relatively high temperatures, more recent examples of hybrid dynamic-permanent networks highlight the possibility to recover deformation up to 80-90 °C in elastomeric materials.[74,75]

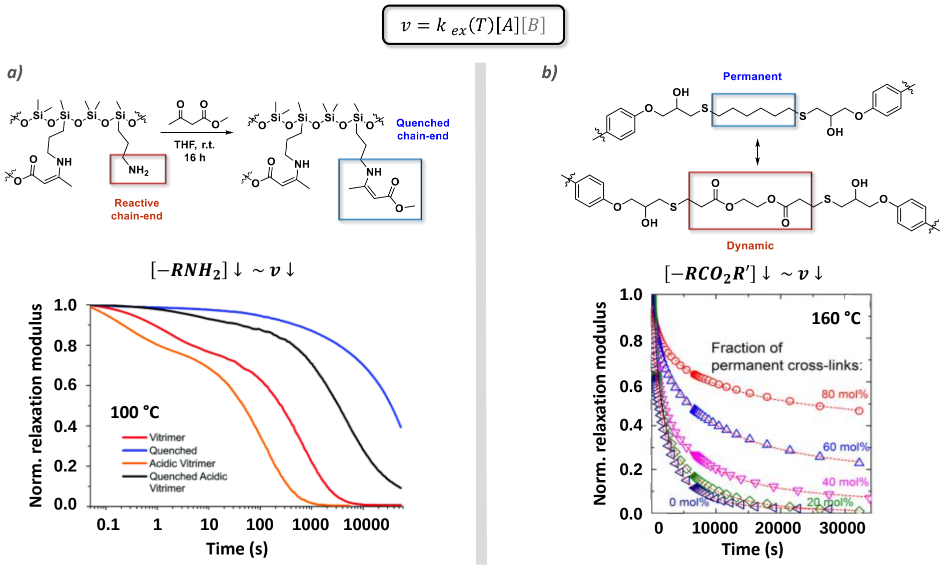


Figure 4. Permanently reducing or blocking the availability of functional groups has an important effect on the rate and extent of material flow: a) Quenching or reacting the necessary primary amine chain-ends for exchange, results in a significant decrease in relaxation rate.[69] (Adapted from ref. 70 with permission from Royal Society of Chemistry, copyright 2017) b) Representation of relaxation behaviour of epoxy-based dynamic covalent networks by substituting a fraction of dynamic cross-links for permanent ones.[70] (Adapted from ref. 71, copyright 2018, with permission from American Chemical Society)

Another appealing strategy for controlling the availability of reactive moieties in a dynamic covalent network is to keep them abundantly present, but limit their diffusion in the rubbery phase. As a result, chemical reactions are less likely and the formation of aggregates or clusters leads to predominant elastic behaviour.[76] For example, when the incompatibility of distinct polymer phases results in phase-separation or nano-structuration, polymer chain association or dissociation is hampered. Heating, on the other hand, promotes the formation of continuous phases, resulting in the (re)activation of dynamic behaviour.[49,77–80] Furthermore, because cooling can cause the polymer phases to re-separate, such nano-structuration has a reversible character.

Intrigued by the uneven distribution or partial confinement of dynamic cross-links in phase separated networks, Ricarte, Leibler and co-workers highlighted the importance of studying the incompatibility effects between the polymer backbone and reactive functional groups.[49,77,81] By grafting polar dioxaborolane units onto a hydrophobic polyethylene backbone, they showed that the exact nature and content of the microphase will primarily determine the level of elasticity or creep resistance that can be achieved (**Figure 5a**). Later, Sumerlin and co-workers investigated the effect of phase separation of block copolymer architectures in order to significantly alter the reactivity of acrylic vinylogous urethane networks.[82] When the flow behaviour was compared at 150 °C, the statistical vitrimer network could relax stresses in 1000 s, while the block copolymer one entered much slower modes of relaxation as a result of more limited chain diffusion. This deviation in flow behaviour at longer time scales was investigated by performing creep experiments at 150 °C with a shift in permanent deformation from 75% (statistical) to 33% (block) (**Figure 5b**). More recently, Kalow and co-workers further investigated the composition of such block copolymer precursors in vinylogous urethane networks to achieve even better organised morphologies.[83] In summary, phase separation and other types of hierarchical structuration are powerful design concepts, especially when introducing (often polar) dynamic cross-links into

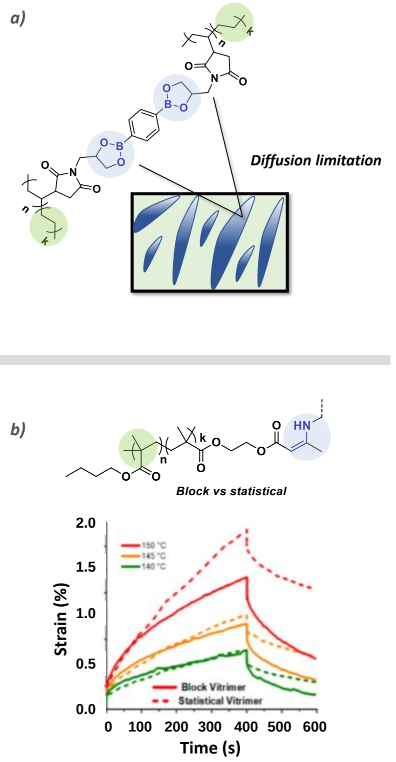


Figure 5. a) Schematic representation of phase separation of dynamic dioxaborolane cross-links and hydrophobic polyethylene backbone.[77] b) Creep recovery plot of acrylic vinylogous urethane networks showing a creep reduction for the phase-separated block compared to the statistical dynamic covalent network.[82] (Adapted from ref. 83, copyright 2020, with permission from American Chemical Society)

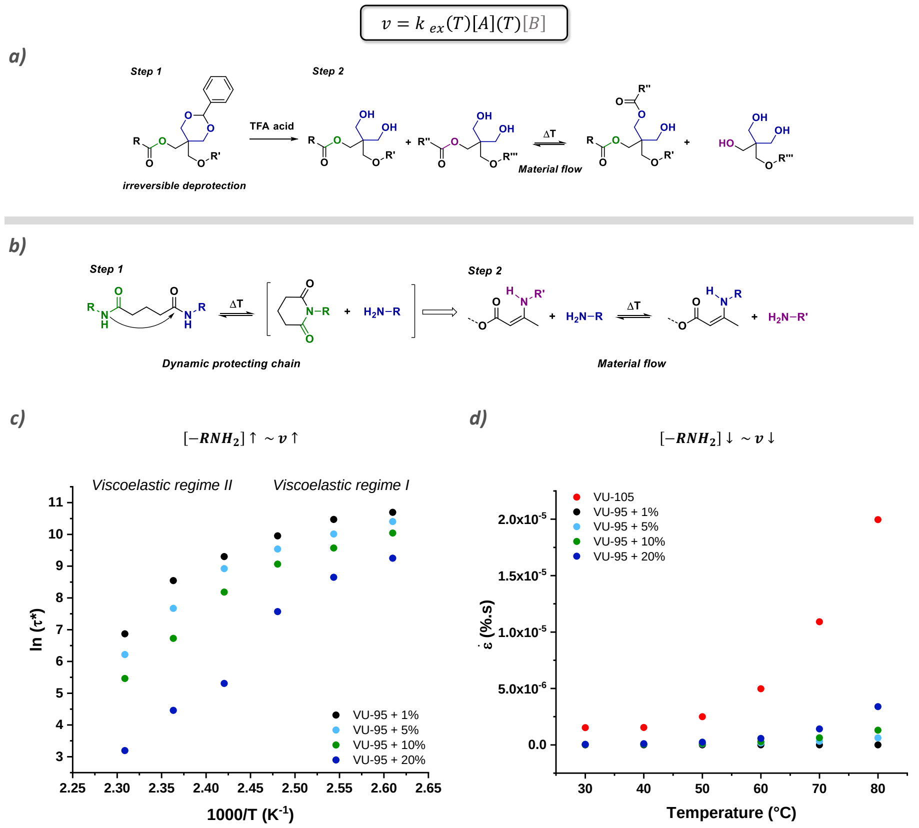


Figure 6. Influence of a) an irreversible and b) a reversible protection-deprotection strategy to generate reactive functional groups for material flow;[50,84] c) Arrhenius plot and d) creep rate as a function of temperature of modified vinylogous urethane dynamic covalent networks displaying dual dynamic behaviour as a function of temperature due to an increased/decreased availability of pendent primary amines upon reversible deprotection/protection. (Adapted from ref. 50 with permission from John Wiley & Sons, copyright 2022)

(often apolar) polyolefin materials. On the other hand further research into mechanical properties and chemical robustness of phase-separated materials is required.

Another method of limiting the exchange of polymer chains is to temporarily protect reactive functional groups. Their chemical modification, in particular, prevents them from participating in a rearrangement reaction. Although not explicitly indicated as such a strategy, Heuts and co-workers reported a simple protection-deprotection strategy to introduce pendant hydroxyl groups in a dynamic polyester network on-demand.[84] When a benzylidene protecting group was irreversibly removed using trifluoro acetic acid (TFA), hydroxyl groups were released, which promoted cross-linking and transesterification reactions (**Figure 6a**). However, due to the selected strategy, creep resistance or significant inhibition of transesterification could not be recovered after deprotection. Very recently, our own group extended this concept by solely using the polymer backbone as a reversible protecting group (**Figure 6b**).[50,85] More specifically, transamination of vinylogous urethane vitrimers could be controlled by thermoreversibly shielding reactive primary amines with another dynamic chemistry. The dynamic masking strategy resulted in elastomeric materials with a reduction in creep rate by a factor of 30-50 at 80 °C in comparison to a benchmark vitrimer material (**Figure 6c and 6d**). In contrast, similar relaxation rates (20-900 s) at 160 °C could be achieved as a result of the release of additional pendent primary amines.

These findings confirm that a strategic monomer selection, driven by chemical intuition, will aid in the further rational design of dynamic covalent networks that are able to switch between an active and inert state. Moreover, we strongly believe that the synergetic effect of dynamic chemistries to promote or inhibit reactivity holds high potential to further tune and control viscoelastic properties, although care should be taken to still yield the desired effect at use temperatures.

3.3. Controlling the proximity of reactive functional groups

Adding a catalyst or using an intrinsically reactive bond to lower the high enthalpic energy barrier for reaction, which inevitably leads to creep, is a traditional method for accessing dynamic behaviour within a reasonable temperature interval. A rather novel approach for the promotion of material flow, while maintaining a high energy barrier, is to rely on mild groups or substituents close to the reactive center.[57,58] This proximity-driven rate enhancing effect is referred to as neighbouring group participation (NGP).[86] For a comprehensive overview on the subject of NGP we refer to previous reviews by our research group and the one of Ladmiral and co-workers as we will limit the discussion in this section to the most important facts and recent examples.[57,58] Fundamentally, NGP makes enthalpically challenging (high barrier) bond exchange reactions more favourable through a significant entropic (statistical) contribution, in theory leading to stronger temperature responses and making

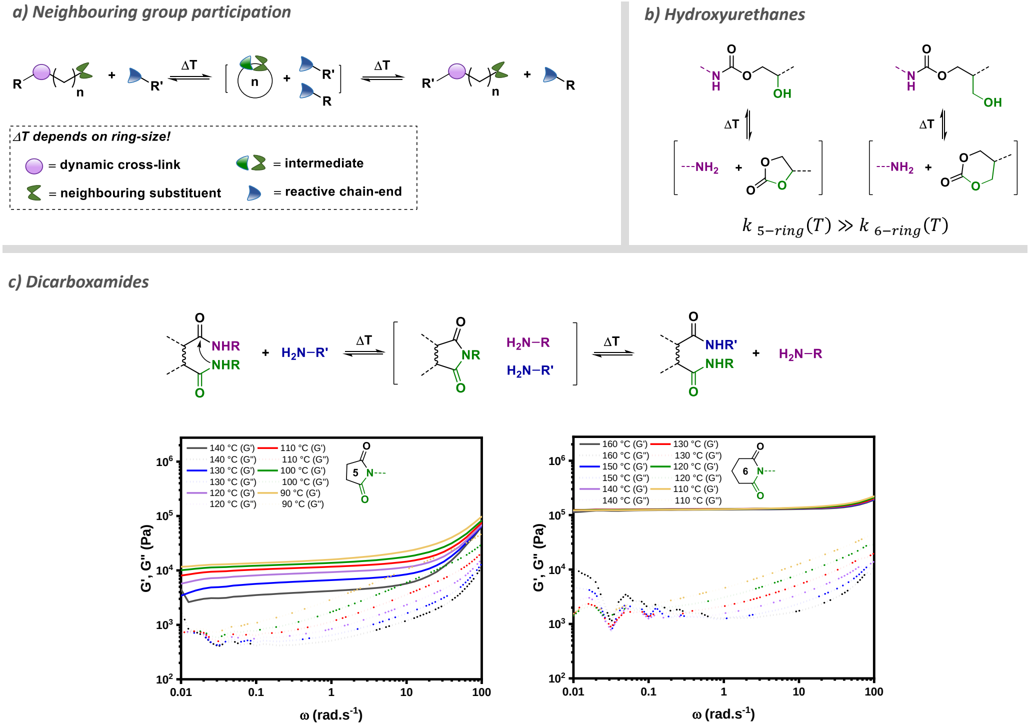


Figure 7. Influence of proximity of neighbouring group to the dynamic cross-link on the onset of material flow: a) Schematic representation of neighbouring group participation (NGP) through covalent bond formation to the reaction centre; b) Nucleophilic NGP of hydroxy groups with a variable distance from a urethane bond, result in cyclic carbonate intermediates of different ring-size and stability;[88,89] c) Nucleophilic NGP of amide groups, displaying the stark contrast in viscoelastic behaviour as a function of spacer length between two neighbouring amides.[90] (Adapted from ref. 90, copyright 2021, with permission from American Chemical Society)

this concept particularly interesting for halting creep. Especially when combined with a robust, otherwise less reactive covalent bond, activation will only occur at higher temperatures when the entropic favour outweighs the enthalpic penalty (cf. Eyring equation).

Since NGP often involves the formation of a cyclic intermediate, the onset of dynamic behaviour will mainly depend on the stability and ease of ring-formation (**Figure 7a**).[87] In their study on reprocessable polyhydroxyurethanes, Dichtel, Hillmyer and co-workers compared the stress-relaxation and thermal stability of networks that involved the formation of five-and six-membered ring intermediates (**Figure 7b**).[88,89] Heating at 180 °C for 15 min revealed that the formation of a five-membered ring was much more likely, but at the expense of several side-reactions. Interested in further exploring the relationship between ring-size of a reactive intermediate and viscoelastic behaviour, our group investigated the effect of NGP in elastomeric polyamides (**Figure 7c**).[90] The formation of a cyclic intermediate required the activation of an amide bond through nucleophilic participation of another neighbouring amide, resulting in a thermally stable imide chain-end. By adjusting the level of NGP, a decrease in creep rate of a factor 2 at 90 °C could be obtained while increasing relaxation by a factor 5 at 165 °C.

An interesting alternative to control the reactivity of a dynamic covalent cross-link, is to rely on light-promoted interference of a neighbouring group that can switch a dynamic bond between an active and inactive state.[59] For example, Hecht and co-workers investigated the reversible photocyclization of a diarylethene group in order to adjust the electrophilicity of an adjacent carbonyl group in a dynamic imine-based polysiloxane network.[91] As a result, due to a 10-fold increase in relaxation rate upon light-driven ring-closure, material flow could only occur at room temperature after UV-irradiation. They later introduced a similar approach using furan-containing diarylethene photoswitches to modulate the reactivity of a furan-maleimide cross-linked polyester network (**Figure 8a**).[92–94] By selectively inhibiting the retro Diels-Alder reaction, after UV-irradiation, no significant material flow could be measured, even after prolonged heating at 120 °C. Subsequently, dynamic behaviour could be restored upon illumination with visible light. With the aim to reversibly introduce a significant shift in the bonding equilibrium, Kalow and co-workers recently investigated the combination of photoswitchable azobenzenes and dynamic boronic esters (**Figure 8b**).[95] Due to the changed proximity of substituents to the dynamic bond upon isomerisation to the (Z)-isomer, a 20-fold increase in association and therefore dimensional stability was observed.

Using mildly reactive functional groups or minor structural and conformational changes to activate or inhibit the dynamic behaviour of polymer networks is an interesting design tool. We believe that additional research will allow for a more fundamental understanding of such chemical reactivity and the incorporation of different levels of NGP into a wide range of (common) polymer matrices. A particular challenge will be to ensure that dynamic covalent bonds are well activated and intrinsically very robust, in order to establish true 'on-off' behaviour and avoid creep.

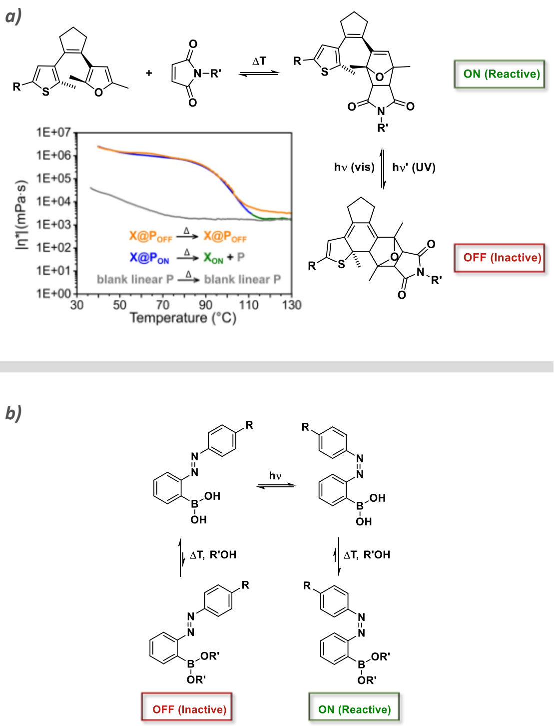


Figure 8. a) Photoswitchable diarylethene-based cross-linker capable of controlling the retro furan-maleimide Diels Alder reaction. Reversible light-driven ring-closure allows switching between an active and inert state as demonstrated by the change in complex viscosity.[92] (Adapted from ref. 93 with permission from Nature research, copyright 2016) b) Photoisomerisation of azobenzenes in a boronic ester network induces conformational changes to tune the thermodynamic equilibrium.[95] (Adapted from ref. 96, copyright 2020, with permission from American Chemical Society)

3.4. Using highly endothermic bond dissociation

If chain fragmentation can occur without the need for polymer chain association (in a dissociative dynamic polymer network), another intriguing strategy is to choose dynamic covalent reactions with an enthalpically unfavourable dissociation but a relatively low activation energy barrier. As such, the generation of dissociated intermediates will only occur at higher temperatures where the enthalpically driving force can no longer compensate for the natural entropic tendency towards chain debonding.[33,60,96,97] In the absence of chain defects, also the exchange of chain bonds is blocked, resulting in intrinsic resistance to permanent deformation during use. Obviously, the success of the employed strategy will also depend on the thermal stability of the intermediate to avoid possible degradation. For example, homolytic chain cleavage into reactive radicals cannot be expected to give rise to durable covalent bond exchange.

An interesting example of highly endothermically dissociating chains are the so-called poly(1,2,3-triazolium) networks reported by Montarnal and Drockenmuller and co-workers.[17,25,98] In light of creep resistance, one important finding from their research is that transalkylation of N-alkylated triazolium salts can only occur when preceded by chain-cleavage induced by the nucleophilic counterion. A large difference in the extent of dissociation at a given temperature could be determined by varying the nucleophilic character of the counterion between Cl^-, Br^-, I^-, and Mesylate$^-$ (**Figure 9a**). Creep experiments confirmed that no significant permanent deformation could be measured below 100 °C. This was also reflected in the relaxation time, which decreased by a factor of 500 at 150 °C for low levels of decross-linking. Nonetheless, further heating would shift the equilibrium toward dissociation while also significantly increasing relaxation, resulting in a steep decrease in viscosity. This contrasts with materials that also have reactive chain defects present at room temperature. The authors also showed that a drastically different relaxation behaviour is obtained when changing the N-substituent from an alkyl to benzyl group as a result of the formation of a more reactive intermediate towards transalkylation reactions (**Figure 9b**).[42] Whether the same S_N2-type alkyl substitution, resulting

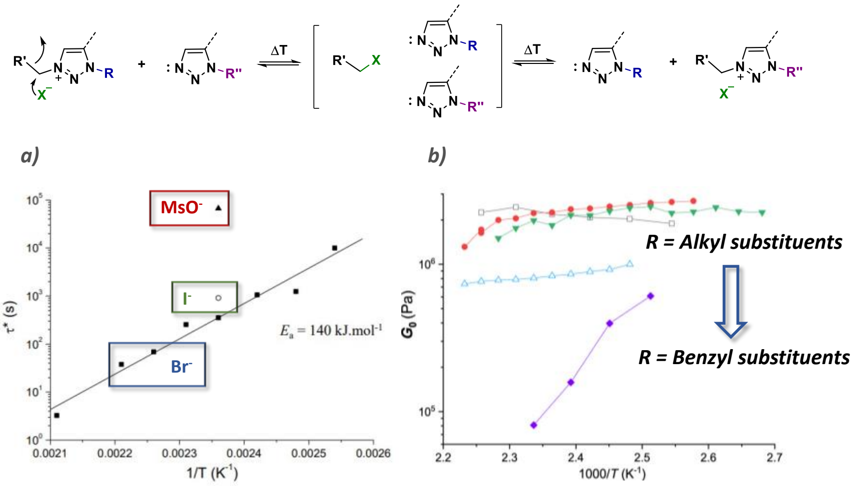


Figure 9. Influence of chemical composition and structure on the dissociation and exchange rate of dynamic triazolium salt containing covalent networks. a) Arrhenius plot of networks with different counterion (X^-) but same cross-link structure.[98] (Adapted from ref. 99 , copyright 2015,with permission from American Chemical Society) b) Relaxation modulus plotted as a function of temperature to highlight the difference in dissociation when changing N-substituents (R) from alkyl to benzyl groups.[42] (Adapted from ref. 42, copyright 2021, with permission from American Chemical Society)

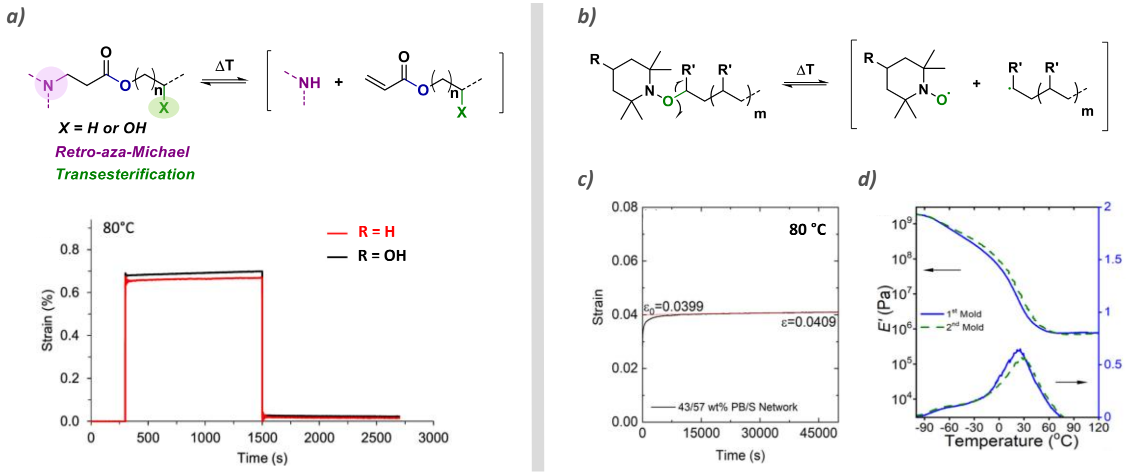


Figure 10. a) β-amino ester-based networks combining a thermally demanding transesterification and dissociation of the Michael-adduct, resulting in low permanent deformation at 80 °C.[102] (Adapted from ref. 90, copyright 2021, with permission from American Chemical Society) b) Radical-mediated dynamic covalent networks as creep-resistant SBR rubbers.[18] c) Creep experiment conducted at 80 °C for 14 h showing no significant permanent deformation. d) Temperature dependency of tensile storage modulus (E'), indicating excellent stability and reprocessability. (Adapted from ref. 17, copyright 2021, with permission from American Chemical Society)

from counterion nucleophilicity, could be integrated into other transalkylation chemistries, such as trialkylsulfonium, anilinium and pyridinium salts,[99–101] is an open research question at this stage.

When revisiting a well-documented chemistry as a source of inspiration to design creep resistant dynamic covalent networks, we recently investigated (retro)-aza-Michael additions for polyester formulations.[102,103] β-amino ester-based networks were synthesised through the aza-Michael addition of commercially available amines and acrylates, whereby the created activated esters promoted both a thermally demanding transesterification and dissociation of the Michael-adduct (**Figure 10a**). However, activation could only occur at elevated temperatures due to the high reaction enthalpy associated with the retro-Michael reaction. This synergy between two dynamic covalent chemistries resulted in a drastically different viscoelastic behaviour when comparing the low permanent deformation of ~0.02 % at 80 °C after 20 min and fast relaxation at 180 °C in ~100 s.

Radical-mediated dynamic covalent networks, where bond dissociation into reactive radicals is obviously enthalpically demanding, offer another interesting dynamic chemistry platform. Because radical addition and fragmentation reactions occur without a true activation energy barrier, relaxation after homolytic cleavage can be very fast upon heating, as long as no competing radical side reactions occur (atom transfer).[33] For instance, Torkelson and co-workers explicitly studied the creep resistant behaviour of TEMPO-based alkoxyamine dissociation in a polybutadiene matrix, giving long-living radical fragments (**Figure 10b**).[18] After 14 h of creep testing at 80 °C, permanent deformation values of 0.09 %, comparable to thermoset materials, were reported (**Figure 10c**). When the temperature was raised from 80 °C to 140 °C, however, full reprocessability could be achieved in 60 min with good property recovery (**Figure 10d**). As an alternative, they later reported the use of dialkylamino disulfide cross-links in polymethacrylate networks.[104] Due to the interesting balance between reactivity and stabilisation of a generated thionitroxide radical, the obtained material displayed permanent deformation of only ~0.07% at 70 °C after 14 h. Moreover, relaxation times of around 100 s could be measured at 150 °C, which highlighted a drastic decrease in viscosity upon heating.

4. Conclusions

In this Minireview we have demonstrated how advantageous short-term and long-term dynamic behaviour in thermosets can be leveraged and should be experimentally validated. Furthermore, because organic materials have much lower thermal stability than inorganic materials, determining the relatively small useful processing window is critical. As a result, by adjusting the nature of the dynamic covalent bond and controlling the availability of catalysts, reactants, and substituents, examples of creep resistant *and* highly dynamic covalent networks are emerging.

While it is not straightforward to compare various reported approaches, we selected reported chemical concepts with the greatest potential (to date) based on factual effects. When referring to the title of this manuscript, we believe that it is not impossible to induce creep resistance without sacrificing reprocessability. To this end, the natural tendency of entropy to overcome high enthalpic contributions upon heating is a powerful design concept, rather than changing the activation barrier for reaction or using intrinsically reactive bonds. This is intriguing because it corresponds primarily to the last two strategies of neighbouring group participation (activation entropy) and highly endothermic bond dissociation (reaction entropy), which have been shown to have the greatest impact. Furthermore, they both rely solely on the selection of appropriate and often readily available building blocks, making the transfer to existing industrial technologies much more likely. In general, we are strongly convinced that new opportunities for strategic monomer selection and rational design of dynamic polymer networks will continue to be reported, driven by the transition towards durable materials.

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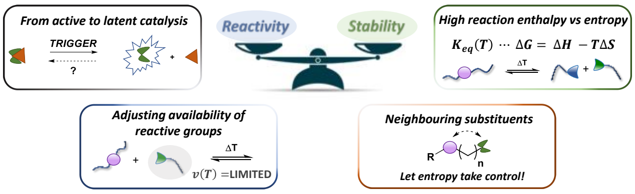

One of the largest challenges in the design of dynamic covalent networks is to balance reactivity during reprocessing with stability during use. In this perspective several strategies are highlighted that combine high processability and creep resistance such as latent catalysis, availability of reactive groups, substituents and intrinsic stability of the dynamic bond.

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