Masked Primary Amines for Controlled Plastic Flow of Vitrimers

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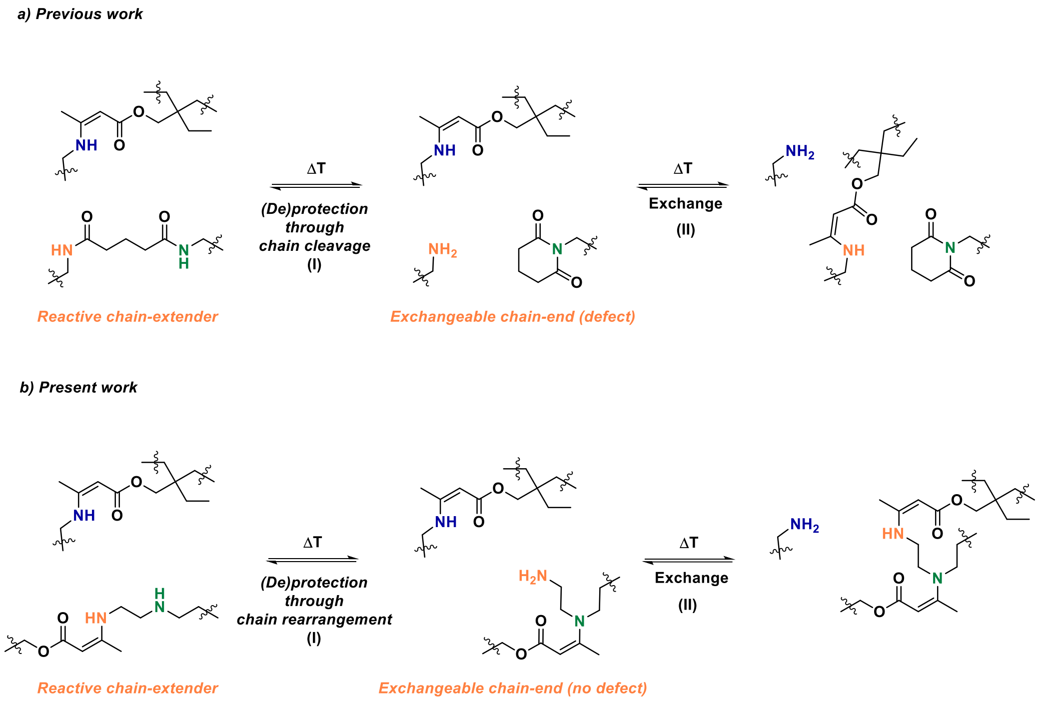
ABSTRACT: We present a simple method for increasing the reprocessability of vinylogous urethane (VU) vitrimers while decreasing the possibility of creep deformation at lower temperatures. In particular, varying amounts of triethylenetetramine were added as co-monomer to the curing VU formulation to ensure that all of the primary amines reacted to form enaminone cross-links, resulting in a network without reactive primary amine chain-ends. As a result, transamination was significantly slowed down because secondary amines are much less reactive to VU exchange. On the other hand, at higher temperatures, pendent primary amines can be released via a dynamic, endothermic exchange with a nearby less reactive secondary amine, thereby (re)activating material flow. As a result, ambivalent viscoelastic behaviour could be achieved without depolymerisation by dynamically releasing pendent primary amines from vinylogous urethane polymer chains. Through careful co-monomer selection, VU vitrimers with low viscosity at processing temperatures and at the same time high viscosity at service temperatures could be prepared without the use of catalysts or additives, leveraging the synergistic effects of mildly reactive functionalities through neighboring group participation.

Thermosets are an important class of cross-linked polymers with everyday applications, ranging from thermal insulation for housing to adhesives and structural components in electronics.[1] Nonetheless, after cross-linking or curing, they have a permanent shape that makes handling, reprocessing, and especially recycling difficult. Vitrimers, on the other hand, are dynamic polymer networks with reactive or triggerable bonds that allow for continuous reshuffling of cross-linking sites to relax external stresses.[2–6] As a result, when heat and pressure are applied, chemical exchange reactions are activated, allowing vitrimers to be welded, reshaped, reprocessed, or recycled without losing network integrity.[7–12] Importantly, this means that the decrease in viscosity of such polymer materials during flow will be primarily determined by the rate and nature of chemical bond exchange.[13,14]

A common diagnostic feature used to distinguish vitrimers from other reversible networks has been their gradual decrease in viscosity as a function of temperature (*i.e.* Arrhenius behaviour) when compared to thermoplastics and dissociative networks.[6,15] As a consequence, vitrimers have good reprocessability over a wide temperature range but at the same time a lower resistance to permanent deformation, *i.e.* creep, during use.[16,17] In contrast, a sharper increase/decrease in viscosity upon cooling/heating is desired for many applications. To meet these requirements, one appealing strategy has been to rely on different exchange reactions,[18–24] or a change in reaction mechanism,[25–28] within the same polymer network. Indeed, synergistic effects between different chemistries can yield a remarkable response to temperature, but careful material design is required to yield the desired effect of inhibiting exchange at lower temperatures.

Recently, our research group combined two dynamic covalent exchange reactions to produce fast reprocessable elastomeric vitrimers with improved creep resistance.[29] Herein, transamination exchange of vinylogous urethane (VU) vitrimers was significantly accelerated when dicarboxamide dissociation resulted in a small degree of depolymerisation, together with the (re)generation of highly reactive free chain-end amines (**Scheme 1a**).[30] Upon cooling, (re)formation of the small fraction of dicarboxamide chain-extender resulted in depletion of available exchangeable groups, which lead to a decrease and eventually shutdown of exchange. In other words, the dicarboxamide motif served as a dynamic protecting group, facilitating the thermal release of the exchange enabling primary amines.[31]

Scheme 1. a) Previously reported dynamic protecting group strategy, relying on the dissociation of dicarboxamide chain-extenders for the release of reactive primary amines in a vinylogous urethane vitrimer.[29,30] b) Reversible (de)protection strategy used in this work, relying on oligoethyleneimines for primary amine release and subsequent transamination.



While fast transamination exchange within VU-based vitrimers is widely reported to critically rely on the presence of free primary amines,[7,25,32,33] the presence of secondary amines in VU networks usually has little effect. Moreover, secondary amines are not appropriate VU monomers, as they do not form stable adducts when reacted with acetoacetates, due to a lack of internal hydrogen bond stabilisation in the resulting VU.[32] However, this general lack of nucleophilic reactivity might be drastically enhanced when a secondary amine group is present in close proximity to a normal VU cross-link.[14,34] In this case, albeit only temporarily, we hypothesised here that a secondary amine may engage a VU linkage as a neighbouring nucleophile (**Scheme 1b**), temporarily releasing a primary amine at elevated temperatures.

In this work, we report the successful implementation of this alternative strategy for the reversible 'in chain' generation of primary amines for vinylogous urethane vitrimers. The obtained materials show high reprocessability at elevated temperatures and an improved resistance to permanent deformation at lower temperatures, when the reactive amines are internally quenched into stable VU bonds. Specifically, commercially available linear oligoethyleneimines were added as a co-monomer to the curing VU formulations, aiming to lock all primary amines into stable VU cross-links. The resulting polymer network does not contain free primary amines, but the unreacted secondary amine groups now serve as a neighbouring functionality that upon heating can undergo a fast chain rearrangement that releases a pendant primary amine. Thus, the spontaneous reversal to the thermodynamically more favoured VU adduct assures the dynamic unmasking and reshielding of primary amines, without making use of an additional dissociative exchange chemistry or any depolymerisation. Various rheology experiments were used to investigate the effect of the co-monomer on vitrimer flow properties, such as stress-relaxation, frequency sweep and creep deformation experiments. In short, a conceptually novel and quite versatile method for the design of VU vitrimers is disclosed, ensuring continuous network integrity.

In order to investigate the feasibility of the proposed strategy, VU formation and transamination studies were initially performed on small molecules. First, methyl acetoacetate was reacted in bulk with an equimolar amount of N-ethylethylenediamine at 80 °C for 4 h. Without further purification, the reaction mixture was quenched with cooled water and submitted for ESI-MS analysis, which revealed primary amine VU formation, which was consistent with previous research,[32,33] and a 'double' VU adduct that could be explained by neighbouring group participation of the secondary amine (**Figure 1a and b**). In other words, although secondary amine transamination reactions are typically slow and thermodynamically unfavourable, the reactivity of the secondary amine here is enhanced entropically, due to the intramolecular nature of the exchange reaction. Thus, the exchange reaction can be assumed to proceed through the formation of a short-lived imidazolidine intermediate.[14,35] Assuming that this process would be more

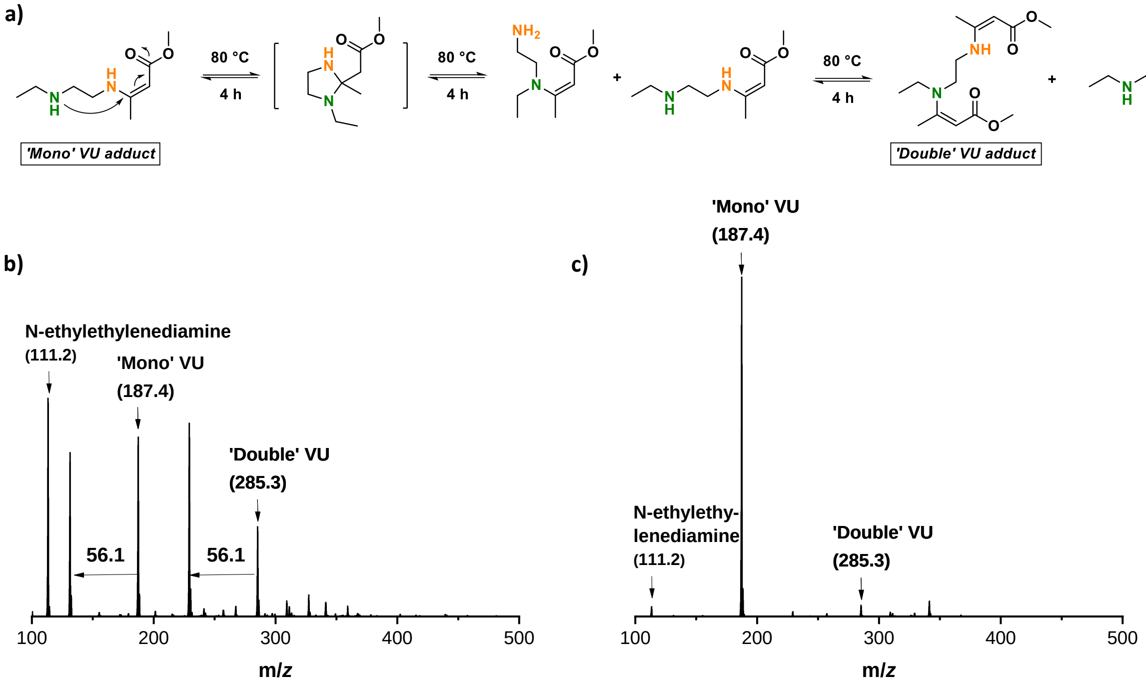


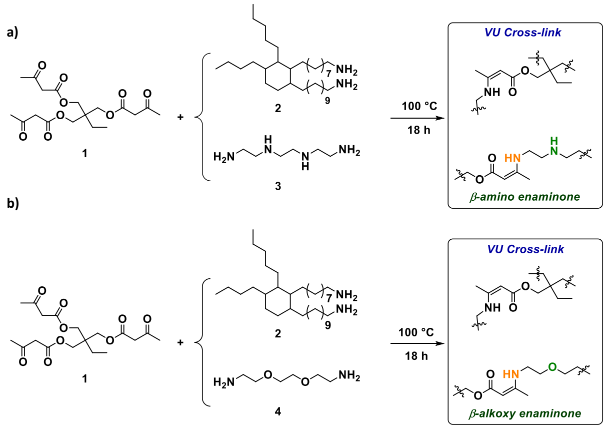
Figure 1. *a) Scheme of the transamination exchange involving a secondary amine acting as a neighbouring group via an imidazolidine intermediate. ESI-MS of the model experiment performed at b) 80 °C for 4 h and c) 25 °C for 24 h.*

pronounced at higher temperatures, the same experiment at 25 °C for 24 h indeed revealed almost none of the 'double' VU adduct being formed (**Figure 1c**). To further strengthen the 'neighbouring group' hypothesis underlying our interpretation of these exchanges, a control experiment was conducted by reacting the acetoacetate compound **1** under the same conditions with an equimolar amount of butylamine and dibutylamine. As expected, ESI-MS analysis indicated complete selectivity for the primary amine VU adduct (**Figure S1**). These initial qualitative results already displayed a distinct reactivity trend of β-amino enaminone compounds, which allowed us to quickly move on to material synthesis.

For vitrimer curing, network formulations were prepared according to a previously reported procedure by reacting trifunctional 1,1,1-trimethyl-propane trisacetoacetate (**1**) and an amine mixture with a stoichiometric ratio of 5 mol% excess acetoacetate groups relative to the primary amines, to minimise the presence of free chain-end amines.[29] First, a reference network (VU-95) was synthesised by solely mixing the trifunctional acetoacetate **1** with Priamine 1074 (**2**). Next, modified materials were made by substituting 5 to 20 mol% of the Priamine 1074 content with triethylenetetramine (TETA, **3**) designated as VU-95 + 5% TETA, VU-95 + 10% TETA and VU-95 + 20% TETA respectively (**Scheme 2a**). As such, β-amino enaminone units were randomly distributed along the polymer backbone and should release the necessary primary amines for exchange upon heating. Furthermore, to ensure that measured changes in material properties did not arise from an enhanced water uptake or changed cross-linking density associated with the more polar TETA compared to Priamine 1074, a separate control material was prepared with 5 mol% of Priamine 1074 substituted by ethylene glycol bis(2-aminoethyl) ether (EGBA, **4**), further referred to as VU-95 + 5% EGBA (**Scheme 2b**).

After the network formation, all samples were shredded into smaller pieces and subsequently compression moulded at 160 °C. Furthermore, ATR-FTIR and swelling experiments were used to characterise network integrity, yielding values that reflect an efficient curing (**Table S1** and **Figure S2**). From DSC analysis, T_g values were obtained in

Scheme 2. Schematic overview of the used curing formulations for modified vinylogous urethane vitrimers. The trifunctional acetoacetate (1) was cured with an amine mixture containing a) triethylenetetramine (3) and b) ethylene glycol bis(2-aminoethyl) ether (4).



the range of -13 to -4 °C, indicative for elastomeric vitrimers (**Figure S3**). Sufficient thermal stability could still be retained, as evidenced by TGA analysis, even after introduction of a relatively large amount of secondary amine groups (**Figure S4**). Moreover, when mimicking (re)processing conditions by performing an isothermal TGA experiment at 160 °C for 2 h, only negligible mass losses could be detected (**Figure S5**).

To determine the changes in dynamic behaviour upon addition of the reactive co-monomer (**3**), stress-relaxation experiments were performed from 160 °C to 110 °C and could be fit to a single exponential decay within reasonable error, which was calculated *via* least squares fitting (**Figure S6-S9**).

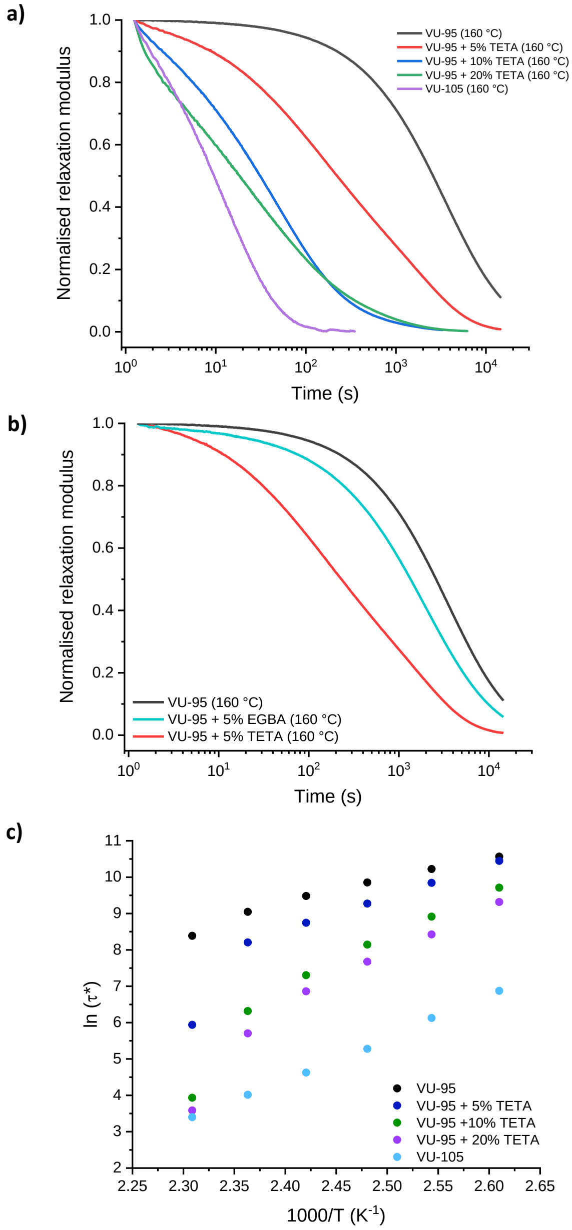


Figure 2. *Normalised stress-relaxation data indicating the impact of introducing a) β-amino enaminone bonds and b) β-alkoxy enaminones on the overall relaxation rate. c) Arrhenius plot of the modified VU vitrimers compared to the reference network.*

A clear dose-responsive acceleration effect could be observed in the comparison of relaxation curves at 160 °C for different added fractions of the reactive co-monomer (**Figure 2a**). In addition, the reference material VU-95, where the presence of pendent primary amines could only be explained by imperfect network formation, did not show complete relaxation while yielding only partially healed samples after reprocessing (**Table S2**).

However, when considering the modified materials, a significantly faster relaxation could be observed when adding only 5 mol% of TETA (4390 s *vs.* 380 s). Moreover, our hypothesis for primary amine release was further supported by the absence of a similar improvement in relaxation rate for VU-95 + 5% EGBA (**Figure 2b**). Further increasing the content of β-amino enaminone bonds resulted in vitrimers with even faster exchange dynamics, i.e. with relaxation time (τ^*) values down to 35 s. This increase in reaction rate was compared to that of a previously reported sample,[29] formulated with 5 mol% excess pendent amines (VU-105), indicating that similar τ^* could be obtained. Importantly, this increase in processability did not come at a (significant) cost of dimensional stability, since relaxation rates of, for instance, VU-95 + 20% TETA only increased with a factor 4 at 110 °C, while a 120-fold increase at 160 °C was observed.

The observed discrepancy in dynamic behaviour as a function of temperature was further visualised when observing the Arrhenius plot in **Figure 2c**. Interestingly, the 'loss of linear Arrhenius behaviour' for the modified vitrimers should not be attributed to an additional dynamic chemistry, nor to a change in the overall exchange mechanism or a drop in network connectivity, but simply to a shift in the availability of reactive primary amines upon heating.[29] To verify this claim, frequency sweep experiments were conducted in the same temperature range to indicate possible changes in cross-linking density or chain mobility (**Figure S10**). All materials displayed a constant plateau modulus (G') as a function of temperature, except VU-95 + 20% TETA. The small variation in G' (above 10 rad.s^{-1}) in the latter case was rationalised by a temporarily larger portion of dangling chain-ends (**Scheme S1**), which are intrinsically non-elastic. Nevertheless, this would not have an effect on the overall number of cross-linking points, but does have an influence on the average cross-linking density. These results demonstrated the existence of an upper limit to the addition of such a reactive co-monomer to still yield a good balance between dynamic, thermal, and mechanical properties as summarised in **Table 1**.

Table 1. Overview of thermal properties and relaxation data of (modified) vinylogous urethane vitrimers.

Vitrimer	T_g[a] (°C)	$T_{d5\%}$[b] (°C)	E_a[c] (kJ.mol^{-1})	$\tau^*_{160\ °C}$[d] (s)	$\tau^*_{110\ °C}$[d] (s)
VU-95	-4	315	58 ± 5	4390 ± 34	38 720 ± 200
VU-105	-15	315	91 ± 2	20 ± 0.3	640 ± 2
VU-95 + 5% TETA	-5	311	75 ± 1	380 ± 8	34 470 ± 84
VU-95 + 10% TETA	-6	305	105 ± 2	50 ± 1	16 500 ± 28
VU-95 + 20% TETA	-13	260	107 ± 2	35 ± 1	11 100 ± 105
VU-95 + 5% EGBA	-5	305	79 ± 4	1955 ± 24	38 340 ± 91

[a] Determined from the second heating in DSC analysis (10 °C.min^{-1}). [b] TGA onset temperatures after 5% weight loss ($T_{d5\%}$). [c] Determined in low temperature region (110 °C to 140 °C) if a non-linear viscosity profile is present, otherwise full temperature region. [d] Obtained from a single exponential fit to the relaxation data. Standard errors were calculated via regression analysis. Note that a larger uncertainty might be present depending on the completeness of relaxation.

Prompted by the interesting viscoelastic behaviour, creep experiments were performed to study the effect of gradually and thermally releasing primary amines on the dimensional stability of the modified vitrimers (**Figure S11**). Measurements were conducted from 30 °C to 100 °C by applying a constant shear stress of 2 kPa over the course of 5000 s. The resulting strain was monitored as a function of time and compared to that of the previously reported VU-105 sample (**Figure S12**).[29] A clear difference in creep behaviour could be observed, e.g. at 90 °C, which was correlated to the availability of the pendent primary amines required for a fast network rearrangement (**Figure 3a**). Moreover, from the slope of the steady-state region (*i.e.* after applying a constant stress for 4000 s), resistance to permanent deformation was assessed by plotting the calculated creep rate ($\dot{\varepsilon}$) as a function of temperature (**Figure 3b** and **Figure S13**). Although there was a significant creep onset for the modified VU vitrimers from 70 °C onwards, absolute creep rates were remarkably lower than for the VU-105 material (**Table S3**). In essence, we were able to combine the processability of a standard VU-105 vitrimer with the increased creep resistance of a VU-95 material.

In summary, creep-resistant vinylogous urethane vitrimers were prepared by simply adding a commercially available oligoethyleneimine co-monomer, which allows the design of an inactive VU vitrimer network in which transamination is hampered by the inaccessibility of free primary amines. Through neighbouring group participation of a nearby secondary amine, VU linkages will behave as free amine defects at high temperatures, giving a clear and significant improvement of the network's rheological properties. This thermal activation occurs without undergoing network depolymerisation, but only through chain

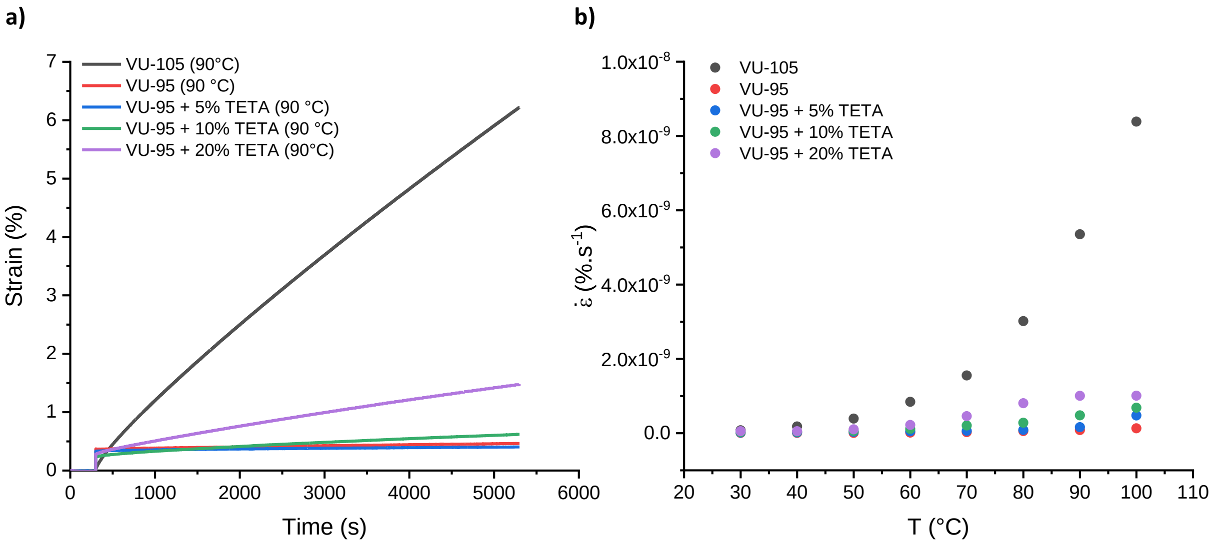


Figure 3. *Creep data of (modified) VU vitrimers with a) representative creep curve at 90 °C and b) creep rate ($\dot{\varepsilon}$) as a function of temperature. Note that some of the data points overlap.*

rearrangements, shifting the network topology towards the release of pendent primary amines. Stress-relaxation experiments revealed drastic changes in exchange rate at elevated temperatures, resulting in a deviation from linear Arrhenius behaviour commonly observed for vitrimers, and approaching – at high temperatures – the dynamic behaviour usually only seen for VU vitrimers with a high degree of free amine network defects. Upon cooling, the primary free amines revert back to the thermodynamically favoured bonds, and cross-linking exchanges are inhibited, resulting in polymer networks with enhanced performance. Furthermore, creep experiments revealed that no significant permanent deformation could be measured for any of the modified vitrimers up to 70 °C. Consequently, these findings confirmed that a strategic monomer selection enabled the rational design of vitrimers with predictable and tuneable properties, greatly expanding their application potential.

ASSOCIATED CONTENT

Supporting Information. Containing IR spectra, DSC and TGA thermograms, stress relaxation data, frequency sweep and creep measurements of reprocessed materials.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

DSC, differential scanning calorimetry; E_a, activation energy; EGBA, ethylene glycol bis(2-aminoethyl) ether; ESI-MS, electrospray ionisation mass spectrometry (ESI-MS); FTIR, Fourier-transform infrared spectroscopy; TETA, triethylenetetramine; TGA, thermogravimetric analyses; T_g, glass transition temperature; THF, tetrahydrofuran; TMP-AA, 1,1,1-trimethylpropane trisacetoacetate; VU, vinylogous urethane.

REFERENCES

(1) Schönthaler, W. Thermosets. In *Ullmann’s Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2000.

(2) Bowman, C. N.; Kloxin, C. J. Covalent Adaptable Networks: Reversible Bond Structures Incorporated in Polymer Networks. *Angew. Chemie Int. Ed.* **2012**, *51* (18), 4272–4274.

(3) Kloxin, C. J.; Bowman, C. N. Covalent Adaptable Networks: Smart, Reconfigurable and Responsive Network Systems. *Chem. Soc. Rev.* **2013**, *42* (17), 7161–7173.

(4) Podgórski, M.; Fairbanks, B. D.; Kirkpatrick, B. E.; McBride, M.; Martinez, A.; Dobson, A.; Bongiardina, N. J.; Bowman, C. N. Toward Stimuli-Responsive Dynamic Thermosets through Continuous Development and Improvements in Covalent Adaptable Networks (CANs). *Adv. Mater.* **2020**, *32* (20), 1906876.

(5) Guerre, M.; Taplan, C.; Winne, J. M.; Du Prez, F. E. Vitrimers: Directing Chemical Reactivity to Control Material Properties. *Chem. Sci.* **2020**, *11* (19), 4855–4870.

(6) Montarnal, D.; Capelot, M.; Tournilhac, F.; Leibler, L. Silica-Like Malleable Materials from Permanent Organic Networks. *Science* **2011**, *334* (6058), 965–968.

(7) Denissen, W.; Rivero, G.; Nicolaÿ, R.; Leibler, L.; Winne, J. M.; Du Prez, F. E. Vinylogous Urethane Vitrimers. *Adv. Funct. Mater.* **2015**, *25* (16), 2451–2457.

(8) Fortman, D. J.; Brutman, J. P.; Cramer, C. J.; Hillmyer, M. A.; Dichtel, W. R. Mechanically Activated, Catalyst-Free Polyhydroxyurethane Vitrimers. *J. Am. Chem. Soc.* **2015**, *137* (44), 14019–14022.

(9) Tretbar, C. A.; Neal, J. A.; Guan, Z. Direct Silyl Ether Metathesis for Vitrimers with Exceptional Thermal Stability. *J. Am. Chem. Soc.* **2019**, *141* (42), 16595–16599.

(10) Lessard, J. J.; Garcia, L. F.; Easterling, C. P.; Sims, M. B.; Bentz, K. C.; Arencibia, S.; Savin, D. A.; Sumerlin, B. S. Catalyst-Free Vitrimers from Vinyl Polymers. *Macromolecules* **2019**, *52* (5), 2105–2111.

(11) He, C.; Shi, S.; Wang, D.; Helms, B. A.; Russell, T. P. Poly(Oxime–Ester) Vitrimers with Catalyst-Free Bond Exchange. *J. Am. Chem. Soc.* **2019**, *141* (35), 13753–13757.

(12) Hendriks, B.; Waelkens, J.; Winne, J. M.; Du Prez, F. E. Poly(Thioether) Vitrimers via Transalkylation of Trialkylsulfonium Salts. *ACS Macro Lett.* **2017**, *6* (9), 930–934.

(13) Winne, J. M.; Leibler, L.; Du Prez, F. E. Dynamic Covalent Chemistry in Polymer Networks: A Mechanistic Perspective. *Polym. Chem.* **2019**, *10* (45), 6091–6108.

(14) Van Lijsebetten, F.; Holloway, J. O.; Winne, J. M.; Du Prez, F. E. Internal Catalysis for Dynamic Covalent Chemistry Applications and Polymer Science. *Chem. Soc. Rev.* **2020**, *49* (23), 8425–8438.

(15) Capelot, M.; Unterlass, M. M.; Tournilhac, F.; Leibler, L. Catalytic Control of the Vitrimer Glass Transition. *ACS Macro Lett.* **2012**, *1* (7), 789–792.

(16) Obadia, M. M.; Jourdain, A.; Cassagnau, P.; Montarnal, D.; Drockenmuller, E. Tuning the Viscosity Profile of Ionic Vitrimers Incorporating 1,2,3-Triazolium Cross-Links. *Adv. Funct. Mater.* **2017**, *27* (45), 1703258.

(17) Li, L.; Chen, X.; Jin, K.; Torkelson, J. M. Vitrimers Designed Both To Strongly Suppress Creep and To Recover Original Cross-Link Density after Reprocessing: Quantitative Theory and Experiments. *Macromolecules* **2018**, *51* (15), 5537–5546.

(18) Chen, M.; Zhou, L.; Wu, Y.; Zhao, X.; Zhang, Y. Rapid Stress Relaxation and Moderate Temperature of Malleability Enabled by the Synergy of Disulfide Metathesis and Carboxylate Transesterification in Epoxy Vitrimers. *ACS Macro Lett.* **2019**, *8* (3), 255–260.

(19) Taplan, C.; Guerre, M.; Du Prez, F. E. Covalent Adaptable Networks Using β-Amino Esters as Thermally Reversible Building Blocks. *J. Am. Chem. Soc.* **2021**, *143* (24), 9140–9150.

(20) Xu, X.; Ma, S.; Feng, H.; Qiu, J.; Wang, S.; Yu, Z.; Zhu, J. Dissociate Transfer Exchange of Tandem Dynamic Bonds Endows Covalent Adaptable Networks with Fast Reprocessability and High Performance. *Polym. Chem.* **2021**,

12 (36), 5217–5228.
(21) Lee, S. H.; Shin, S. R.; Lee, D. S. Self-Healing of Cross-Linked PU via Dual-Dynamic Covalent Bonds of a Schiff Base from Cystine and Vanillin. *Mater. Des.* **2019**, *172*, 107774.
(22) Wright, T.; Tomkovic, T.; Hatzikiriakos, S. G.; Wolf, M. O. Photoactivated Healable Vitrimeric Copolymers. *Macromolecules* **2019**, *52* (1), 36–42.
(23) Yang, Y.; Song, Q.; Li, C.; Tan, J.; Xue, Y.; Su, Z.; Zhang, G.; Zhang, Q. Reprocessable Epoxy Resins Based on Hydroxy-Thioester and Thiol-Thioester Dual Exchanges. *Ind. Eng. Chem. Res.* **2020**, *59* (11), 4936–4944.
(24) Fortman, D. J.; Snyder, R. L.; Sheppard, D. T.; Dichtel, W. R. Rapidly Reprocessable Cross-Linked Polyhydroxyurethanes Based on Disulfide Exchange. *ACS Macro Lett.* **2018**, *7* (10), 1226–1231.
(25) Denissen, W.; Droesbeke, M.; Nicolaÿ, R.; Leibler, L.; Winne, J. M.; Du Prez, F. E. Chemical Control of the Viscoelastic Properties of Vinylogous Urethane Vitrimers. *Nat. Commun.* **2017**, *8* (1), 14857.
(26) Podgórski, M.; Spurgin, N.; Mavila, S.; Bowman, C. N. Mixed Mechanisms of Bond Exchange in Covalent Adaptable Networks: Monitoring the Contribution of Reversible Exchange and Reversible Addition in Thiol–Succinic Anhydride Dynamic Networks. *Polym. Chem.* **2020**, *11* (33), 5365–5376.
(27) Fortman, D. J.; Brutman, J. P.; Cramer, C. J.; Hillmyer, M. A.; Dichtel, W. R. Mechanically Activated, Catalyst-Free Polyhydroxyurethane Vitrimers. *J. Am. Chem. Soc.* **2015**, *137* (44), 14019–14022.
(28) Fortman, D. J.; Brutman, J. P.; De Hoe, G. X.; Snyder, R. L.; Dichtel, W. R.; Hillmyer, M. A. Approaches to Sustainable and Continually Recyclable Cross-Linked Polymers. *ACS Sustain. Chem. Eng.* **2018**, *6* (9), 11145–11159.
(29) Van Lijsebetten, F.; De Bruycker, K.; Spiesschaert, Y.; Winne, J. M.; Du Prez, F. E. Suppressing Creep and Promoting Fast Reprocessing of Vitrimers with Reversibly Trapped Amines. *Angew. Chemie Int. Ed.* **2022**, *61* (9).
(30) Van Lijsebetten, F.; Spiesschaert, Y.; Winne, J. M.; Du Prez, F. E. Reprocessing of Covalent Adaptable Polyamide Networks through Internal Catalysis and Ring-Size Effects. *J. Am. Chem. Soc.* **2021**, *143* (38), 15834–15844.
(31) Kovaříček, P.; Meister, A. C.; Flídrová, K.; Cabot, R.; Kovaříčková, K.; Lehn, J. M. Competition-Driven Selection in Covalent Dynamic Networks and Implementation in Organic Reactional Selectivity. *Chem. Sci.* **2016**, *7* (5), 3215–3226.
(32) Spiesschaert, Y.; Danneels, J.; Van Herck, N.; Guerre, M.; Acke, G.; Winne, J.; Du Prez, F. Polyaddition Synthesis Using Alkyne Esters for the Design of Vinylogous Urethane Vitrimers. *Macromolecules* **2021**, *54* (17), 7931–7942.
(33) Guo, X.; Gao, F.; Chen, F.; Zhong, J.; Shen, L.; Lin, C.; Lin, Y. Dynamic Enamine-One Bond Based Vitrimer via Amino-Yne Click Reaction. *ACS Macro Lett.* **2021**, 1186–1190.
(34) Nishimura, Y.; Chung, J.; Muradyan, H.; Guan, Z. Silyl Ether as a Robust and Thermally Stable Dynamic Covalent Motif for Malleable Polymer Design. *J. Am. Chem. Soc.* **2017**, *139* (42), 14881–14884.
(35) Ferm, R. J.; Riebsomer, J. L. The Chemistry of the 2-Imidazolines and Imidazolidines. *Chem. Rev.* **2002**, *54* (4), 593–613.

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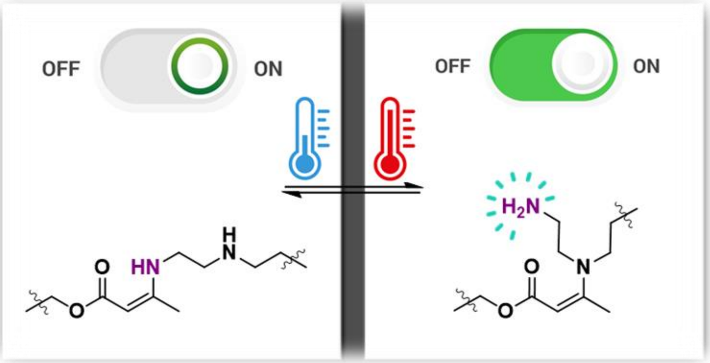

A reversible ‘in chain’ deprotection strategy was used to control dynamic behaviour of vinylogous urethane vitrimers without depolymerization, allowing to suppress creep upon cooling and (re)activate material flow upon heating.