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# Vinylogous Urethane Vitrimers

*Wim Denissen, Guadalupe Rivero, Renaud Nicolaÿ, Ludwik Leibler, Johan M. Winne,\* and Filip E. Du Prez\**

Vitrimers are a new class of polymeric materials with very attractive properties, since they can be reworked to any shape while being at the same time permanently cross-linked. As an alternative to the use of transesterification chemistry, we explore catalyst-free transamination of vinylogous urethanes as an exchange reaction for vitrimers. First, a kinetic study on model compounds reveals the occurrence of transamination of vinylogous urethanes in a good temperature window without side reactions. Next, poly(vinylogous urethane) networks with a storage modulus of ≈2.4 GPa and a glass transition temperature above 80 °C are prepared by bulk polymerization of cyclohexane dimethanol bisacetoacetate, *m*-xylylene diamine, and tris(2-aminoethyl)amine. The vitrimer nature of these networks is examined by solubility, stress-relaxation, and creep experiments. Relaxation times as short as 85 s at 170 °C are observed without making use of any catalyst. In addition, the networks are recyclable up to four times by consecutive grinding/compression molding cycles without significant mechanical or chemical degradation.

## 1. Introduction

Polymer materials are classically subdivided in two main classes, thermosets and thermoplastics, according to their thermal behavior. The first synthetic thermosets for practical applications were invented in 1907 by Baekeland through the combination of formaldehyde and phenol.[1] The resulting highly cross-linked network produced a rigid material that does not soften when heated, and which was called "the material of a thousand uses"[2] due to its versatility. Today, thermosets are used for many demanding applications because of their dimensional stability, creep resistance, chemical resistance, and stiffness. Due to their molecular architecture, thermosets cannot be reshaped, processed, or recycled after full curing. In contrast, thermoplastics can flow upon heating, enabling multiple and easy processing, such as by extrusion,[3] as well as recycling in many cases.[4] Designing polymer systems that combine the benefits of traditional thermosets with the "plastic" properties to facilitate processing is therefore a challenge that has recently attracted great interest.

A way to make the combination of these properties is offered by the introduction of exchangeable chemical bonds into a polymer network, leading to dynamic cross-links. These bonds should be able to rearrange themselves in a reversible manner, providing on a molecular level a mechanism for macroscopic flow without risking structural damage. Polymer networks containing such exchangeable bonds, also known as covalent adaptable networks or CANs,[5] may be further classified into those relying on respectively dissociative and associative exchange reactions.[6]

The most common "dissociative" group of CANs relies on a reversible covalent bond formation between two groups attached to the polymer chains. By triggering the reversed bond forming step (bond dissociation), the material can achieve topology rearrangements (stress relaxation and flow), simply because of a decrease in connectivity during the temporary depolymerization, resulting in a strong and sudden viscosity drop and a loss of dimensional stability. Such systems will always present a sol/gel transition and can thus be solubilized in the presence of solvent. A representative example of a thermally triggered dissociative CAN relies on the well-known reversible Diels–Alder reaction between furans and maleimides.[7]

A less common type of CAN makes use of associative bond exchanges between polymer chains,[8] in which the original cross-links between polymer chains are only broken once a bond to another (part of the) polymer chain has been formed. As a result, such systems can change their topology with no loss of connectivity during the dynamic reorganization process, making such networks effectively permanent and insoluble, even at (very) high temperatures. Interestingly, as with all chemical reactions, the rate of this associative exchange increases with the temperature, leading to an Arrhenius-like viscosity dependence, rather than a sudden and marked viscosity drop at the sol/gel transition. Thermally triggered associative CANs have been coined vitrimers,[9] because of their unique combination of insolubility and gradual thermal viscosity behavior,

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which makes these permanent polymer networks processable like traditional glass.

In 2011, some of the co-authors introduced and demonstrated the unique properties of vitrimer materials using transesterification chemistry in an epoxy-based resin, cross-linked with di- and tri-carboxylic acids. Addition of a mild Lewis acid catalyst, like zinc acetate, to these classical resins resulted in an insoluble material that combined the desired mechanical properties, like classical hard epoxy resins, with the ability to be reshaped and reprocessed after full curing.[9,10] Since then, several other systems have been explored as possible vitrimer materials. Altuna and co-workers were able to produce citric acid-based polyester networks capable of some stress-relaxation in the absence of a catalyst (internally catalyzed by unreacted carboxylic acids), but these materials could not achieve full stress relaxation.[11] Other polyester network and catalyst combinations have also been explored.[12] Vitrimer(-like) materials have also been reported based on olefin[13] or disulfide[14] metathesis reactions. Although different chemistries have been explored for vitrimer materials, the reported materials are somewhat limited in scope and their mechanical properties are often not comparable to those of commercial resins or typical engineering polymers.[12,15]

As an alternative to the use of the now well-known transesterification exchange reactions in vitrimers, we first wanted to explore the possibilities of transamidation reactions. On the one hand, the amide group is thermodynamically more favored as compared to the ester group, which facilitates polyamide synthesis and also makes the polymer less susceptible to decompositions such as hydrolysis, which should open up novel applications for vitrimer materials. On the other hand, amides are also much less reactive than esters, and transamination can only be effected by air- and moisture-sensitive catalysts that are also incompatible with many other functional groups.[16] Thus, we decided to explore vinylogous amides as an interesting related functional group, which combines the thermodynamic and hydrolytic stability of amides—vinylogous amides can be prepared in water as a solvent—with the high intrinsic reactivity of a Michael acceptor through facile conjugate nucleophilic addition of an amine group. In fact, vinylogous amides, as well as the related vinylogous urethanes, are known to undergo associative transamination reactions at elevated temperatures (>100–120 °C), even without a catalyst[17] (**Figure** 1).



X = CH$_2$: vinylogous amide
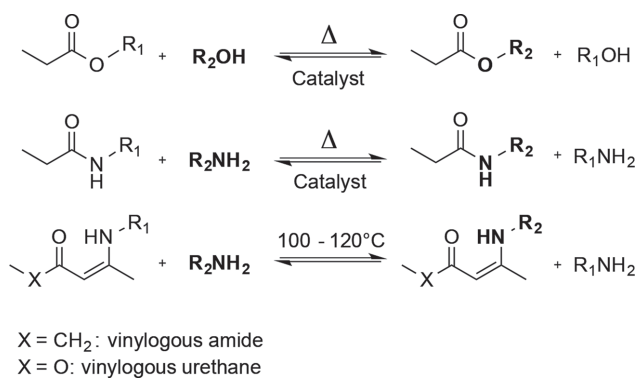X = O: vinylogous urethane

**Figure 1.** Schematic representation of transesterification, transamidation, and transamination of vinylogous amides or urethanes.

The thermal exchange reaction of amines on vinylogous amide-type substrates has been reported on low molecular weight (MW) molecules in only a few studies,[17] and has not received a lot of attention for potential applications. Quite recently, Pomposo and co-workers reintroduced vinylogous urethanes as a "forgotten" dynamic covalent bond in polymer chemistry for the introduction of exchangeable and reversible links in single chain polymer nanoparticles.[18]

In this paper, we report the simple synthesis of a catalyst-free vitrimers, based on the transamination reactions of vinylogous urethanes. To our knowledge, this is the first report on catalyst-free vitrimers. These polyurethane-like materials are readily prepared by the bulk polymerization of easily accessible chemicals and exhibit a $T_g$ above 80 °C as well as excellent mechanical properties. These materials are also insoluble and show very short relaxation times at elevated temperatures, without requiring any additives or catalysts. We further demonstrate that these poly(vinylogous urethane) networks can be recycled several times, by grinding and remolding, without affecting the mechanical properties.

## 2. Results and Discussion

### 2.1. Model Compound Study

Confronted with the difficulties of incorporating vinylogous amide functions into polymer networks, for which no cheap or commercially available building blocks are available, we decided to focus our attention primarily on the amine exchange reactions of vinylogous urethanes. Vinylogous urethanes can be easily prepared in large scale by mixing amines and acetoacetyl esters, while these latter components can be produced by simple acetoacetylation of various polyol building blocks or materials, giving ready access to useful polyacetoacetate monomers and polymers.

In order to assess the kinetics of the conjugate transamination of vinylogous urethanes, a detailed study on low-MW model compounds was conducted. For this purpose, *N*-butyl vinylogous urethane **1** and *N*-benzyl vinylogous urethane **3** were prepared by condensation of propyl acetoacetate with butylamine and benzylamine, respectively.[19,20] After mixing the butyl model compound **1** with 5 equivalents of benzylamine **2** in deuterated benzene (**Figure 2**), the resulting mixture was heated to 100, 120, and 140 °C, and $^1$H-NMR spectra were recorded at different time intervals. The amine exchange reaction could be easily followed by monitoring the well-resolved signals of compounds **1** and **3** (Figure S1, Supporting Information).

In Figure 2b, the remaining fraction of compound **1** is plotted against the reaction time. At low conversions, i.e., under pseudo-first order conditions, a linear decay is observed. At higher conversions, the reaction evolves slowly to a chemical equilibrium, as the backward reaction becomes more important[21]. An activation energy of 59 ± 6 kJ $M^{-1}$ was calculated for the exchange reaction (see Figure S2, Supporting Information). For comparison, this value is approximately 20 kJ $M^{-1}$ lower than that of the transesterification reactions catalyzed by Zn(OAc)$_2$ or Sn(Oct)$_2$[10a,12] in polyester-based vitrimers.

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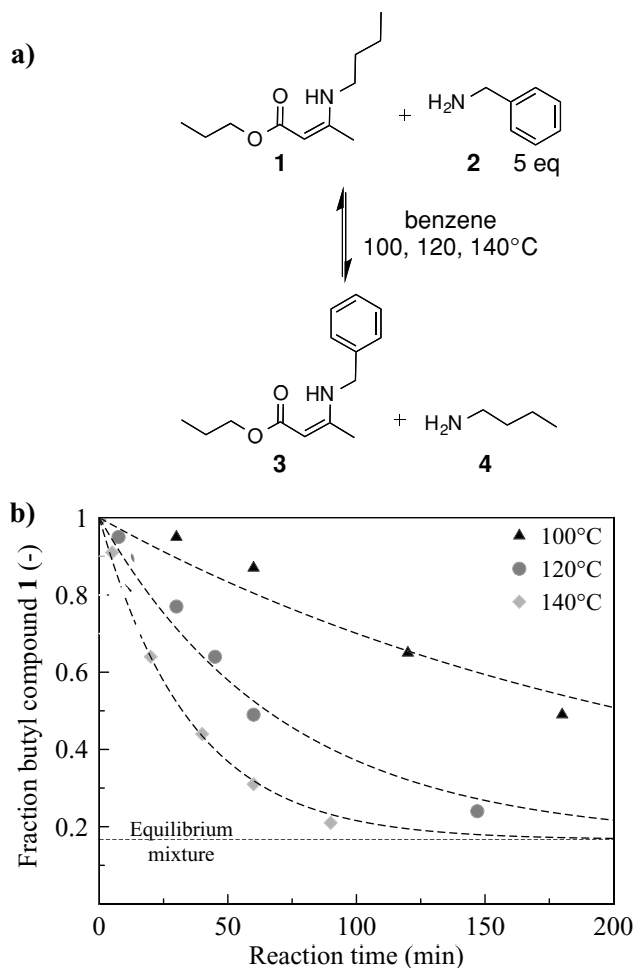www.afm-journal.de

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a)



b)



**Figure 2.** a) Exchange reaction of low-MW model compounds for the kinetic study. b) Disappearance, through exchange reactions, of the butyl model compound **1** as a function of time for different temperatures.

The low-MW model vinylogous urethanes **1** and **3** were also used to verify the thermal stability of these groups under conditions that would mimic thermal treatment of a bulk material. Side reactions could indeed result in decomposition or irreversible cross-links, which would both be detrimental for the envisaged material properties. Reassuringly, model compound **3** showed no significant changes after 14 h of treatment at 150 °C with an excess of amine (Figure S3, Supporting Information).

## 2.2. Vitrimer Synthesis and Characterization

### 2.2.1. Synthesis

Vinylogous urethane networks were prepared using the well-known condensation reaction between acetoacetates and amines. A range of bisacetoacetate monomers can be easily prepared from readily available diol monomers.[22] Combination of these monomers with various commercial available polyamine monomers gives access to a wide choice of poly(vinylogous urethane) polymers, which can be tuned according to the targeted material properties by varying the monomers and the
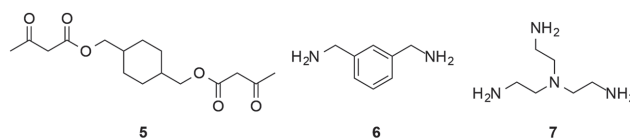


**Figure 3.** Monomers used for vitrimer preparation. A small excess of amines was used in order to keep residual free amines in the cross-linked material.

stoichiometry. Aiming for a material with good mechanical properties and a high $T_g$, and following a brief screening of various possible building blocks, the conformationally rigid cyclohexane dimethanol bisacetoacetae (CDM-AA) **5** and m-xylylene diamine **6** were identified as preferred monomers, with the bulk chemical tris(2-aminoethyl)amine (TREN) **7** as a suitable trifunctional monomer to obtain networks (**Figure 3**).

The condensation reaction between amines and acetoacetates readily occurs at room temperature but generates one equivalent of water that needs to be removed. Thus, the networks were slowly cured as a film at 90 °C over a 24 h period and were then postcured for 30 min at 150 °C to ensure full curing and dryness. In this way, defect-free samples could be obtained. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) confirmed the conversion of acetoacetates to vinylogous urethanes with the disappearance of the ester and ketone bands at 1724 and 1700 cm$^{-1}$, respectively, and the appearance of the C=C and C=O bands of the vinylogous urethane at 1640 and 1604 cm$^{-1}$, respectively (Figure S4, Supporting Information).[23]

In the prepared poly(vinylogous urethane) networks, the stoichiometry of the functional groups is a crucial factor, since the availability of sufficient free amines is absolutely essential for a fast reorganization process through the envisaged transamination reaction. On the other hand, preparing a network with pending free amines implies working under nonstoichiometric conditions, which affects the gel point conversion as well as the network topology. In order to find an optimal compromise, three compositions with a constant theoretical gel point of 0.83, calculated according to the formula of Flory–Stockmayer,[24] and a stoichiometric ratio [R = (equivalent acetoacetate)/(equivalent amine)] of 1, 0.95, and 0.90 were initially studied. As expected, the obtained networks showed significant swelling but did not dissolve in N-methylpyrrolidone, even when heated for 24 h at 100 °C, well above the glass transition temperature of these materials (vide infra). As expected too, similar treatment, but with additional benzyl amine in the solvent, resulted in a complete dissolution of the material due to amine exchange reactions and thus to depolymerization (Figure S5, Supporting Information). This experiment already indicates a quickly operating amine exchange reaction in these materials.

As can be observed from **Table 1**, materials with more free amines also show a higher swelling ratio, which can be attributed to the increase in network defects.

As expected, these defects also increased the soluble fraction. Without a significant excess of amines, however, very little amines would be available for network reorganization. Therefore, a stoichiometric ratio of 0.95 was chosen as a good compromise for these initial studies, with ample free amines to facilitate exchange whilst having an acceptable soluble fraction. This

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**Table 1.** Swelling ratio and soluble fraction in NMP (100 °C, 24 h) for different stoichiometric ratios [R = (equivalent acetoacetate)/(equivalent amine)].

| R | Swelling ratio [%] | Soluble fraction[a] [%] |
|---|---|---|
| 0.90 | 750 | 25 |
| 0.95 | 590 | 11 |
| 1.00 | 390 | 4 |

[a]Determined after 24 h, at which time samples showed no more significant increase in soluble fraction (see Figure S13, Supporting Information).

somewhat off-stoichiometric ratio was also expected to result in a more reproducible amount of actual free amines in the bulk material. Indeed, a large variation in material properties could result from small, unavoidable deviations of stoichiometry in a R = 1.00 network, which would make the initial studies and characterization of these novel materials difficult.

### 2.2.2. Characterization

*Thermal Analysis*: The bulk polymerization of CDM-AA, *m*-xylylene diamine, and TREN yielded a glassy network at room temperature with excellent mechanical properties, evidenced by a glass transition temperature of ≈87 °C (Figure S6, Supporting Information), a storage modulus of ≈2.4 GPa (Figure S7, Supporting Information) and stress at break of ≈90 MPa (see further Figure 6b). Dynamic mechanical analysis (DMA) confirmed the presence of a network with a rubbery plateau of 10 MPa. By thermogravimetric analysis (TGA), the vinylogous urethane networks proved to have good thermal stability with a mass loss of 2.5% at 287 °C (295 °C under nitrogen atmosphere) (Figure S8, Supporting Information).

Since the materials are expected to withstand elevated temperatures for longer periods when being processed, isothermal TGA was also conducted (Figure S9, Supporting Information). The weight loss after 2 h at 150 °C and 180 °C is negligible (<0.5%) and comparable to that of a commercial epoxy (EPON 828 cured with DETA,[25] indicating that the vinylogous urethane networks are stable when heated during a reasonable timeframe.

*Rheology*: The flow properties of the vinylogous urethane networks were studied by stress–relaxation and creep experiments. For the stress–relaxation, a torsional strain of 1% was applied and the relaxation modulus was monitored as a function of time. As shown in **Figure 4**a, full stress–relaxation was observed at all temperatures. This behavior is in accordance with a viscoelastic fluid, further indicating that no nonexchangeable cross-links were introduced during the curing step or stress–relaxation experiment.

Based on the Maxwell model for viscoelastic fluids, relaxation times were determined at 37% (1/e) of the normalized relaxation modulus. These relaxation times range from 550 s at 130 °C to 85 s at 170 °C. Taking into account the absence of catalyst and the rather rigid polymer structure, no other permanently cross-linked systems or vitrimers exhibit such a fast relaxation to our knowledge. This characteristic likely reflects the very high density of vinylogous urethanes in the network
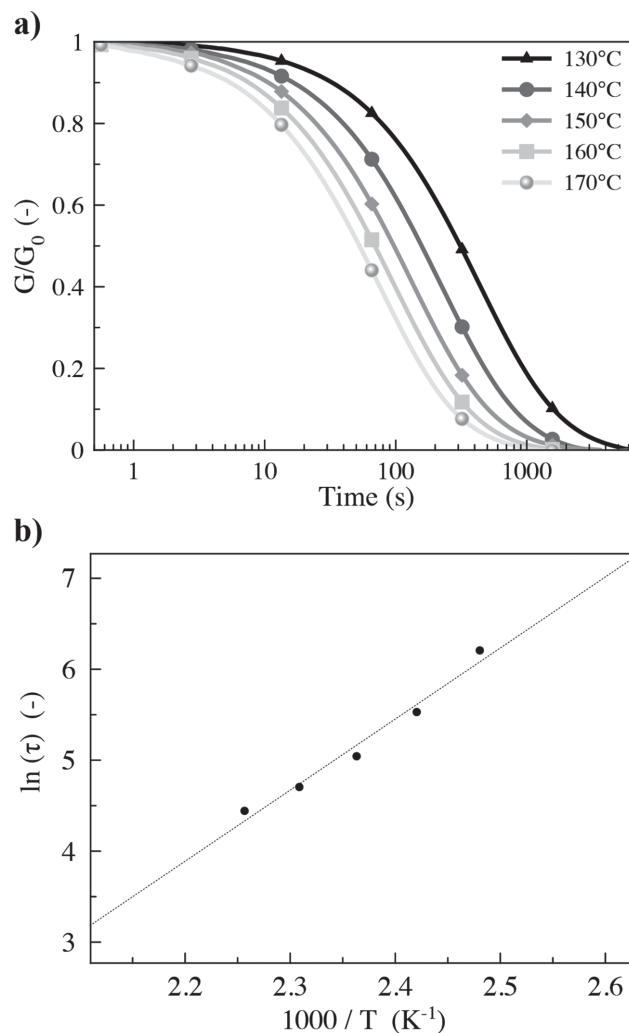


**Figure 4.** a) Normalized stress–relaxation curves at different temperatures. b) Fitting of the relaxation times to the Arrhenius equation.

and the low activation energy for exchange (vide supra). Since the relaxation times are controlled by the associative exchange reactions, the temperature dependence of the relaxation time can be described by the Arrhenius equation[26] (Equation (1))

$$\tau(T) = \tau_0 \exp\left(\frac{E_a}{RT}\right) \tag{1}$$

As shown in Figure 4b, the relaxation times indeed follow the Arrhenius law, and an activation energy of (60 ± 5) kJ M$^{-1}$ was calculated from the slope. This result is in very good agreement with the activation energy obtained for the model compounds.

A key characteristic of vitrimers is the topology freezing transition temperature, $T_v$, that corresponds to the transition from the solid to the liquid state, as a result of exchange reactions within the polymeric network.[10] This transition is conventionally chosen as the temperature where the viscosity reaches $10^{12}$ Pa s,[27] and for the material used in our rheology study (Figure 4), the value of $T_v$ can be extrapolated from the Arrhenius fitted line to a relaxation time of $3 \times 10^5$ s.[28] This

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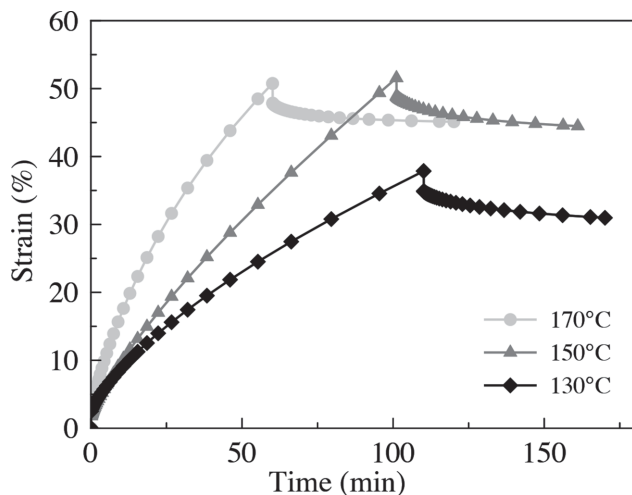MATERIALS
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**Figure 5.** Elongational creep of the vinylogous urethane network with an applied stress of 0.1 MPa at different temperatures.

extrapolation results in a hypothetical $T_v$ of 29 °C for this material, which is below its $T_g$ of 87 °C (vide supra). In practice, when the temperature is lowered towards the $T_g$ of a polymer, chain relaxation processes become slower because segmental motions are arrested due to free volume density changes. Thus, the stress relaxation becomes a more complex process, and quenching of the network topology is coupled to the quenching of segmental motions. When the system is cooled, the increase of mechanical relaxation times is dominated by glass transition effects because of the non-Arrhenius (Williams–Landel–Ferry (WLF)) nature of the relaxation time increase. On the other hand, on heating, the decrease of relaxation times (viscosity) is at some point essentially governed by topology changing exchange reactions. For these materials with very short molecular relaxation times, $T_v$ does not exist since the topology of the network is frozen below the glass transition, which concomitantly arrests all exchange reactions that could result in network topology changes.

In accordance with stress–relaxation experiments, creep experiments also confirmed that the vinylogous urethane networks behave like a viscoelastic liquid at elevated temperatures. **Figure 5** depicts the results of elongational creep experiments at different temperatures. Following the initial elastic response, primary creep with a rapid rate decrease is observed. Then, a steady state is reached, characterized by a constant creep rate. When the stress is released, the material recovers only its initial elastic response and a permanent deformation remains. The networks were easily deformed up to 45% without rupture over a broad temperature range. These results clearly show that these vinylogous urethane-based vitrimers can be processed without a precise control of the temperature, in strong contrast to the strict conditions required for processing of thermoplastics.

*Recycling*: The recyclable nature of the networks was examined by first grinding the samples into particles that were used as raw substance for compression molding (**Figure 6**a). To ensure the reversibility, the procedure was repeated four times and the recycled samples were subjected to tensile tests, dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), solubility experiments, and ATR-FTIR
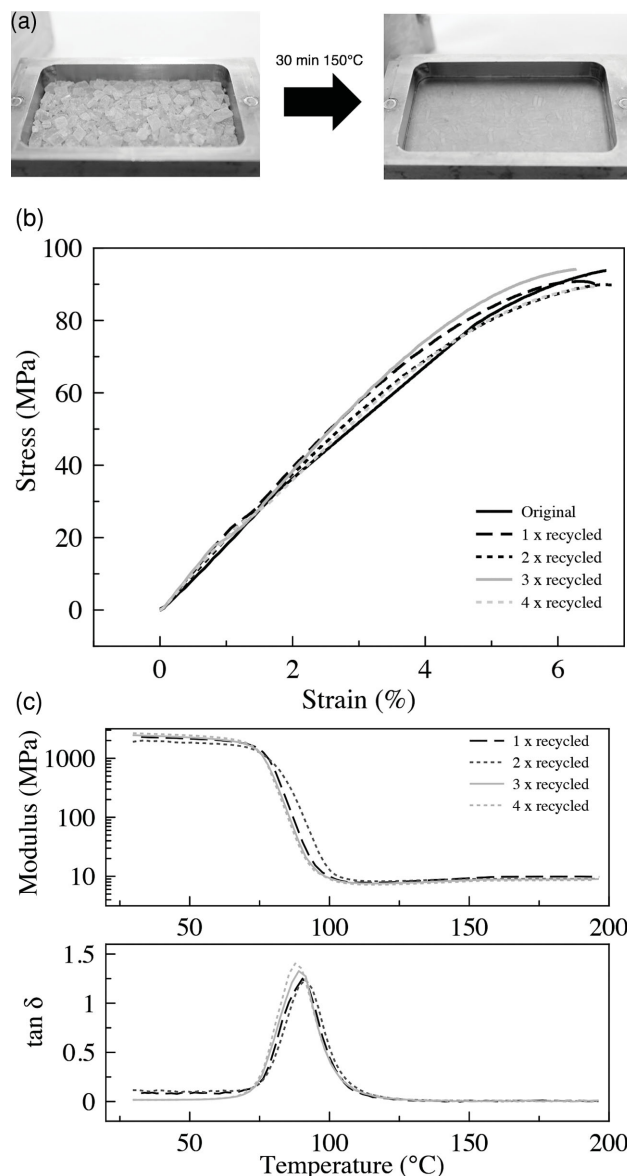


**Figure 6.** a) Recycling of the grinded polymer network by compression molding. b,c) Stress–strain curves and DMA of the recycled samples demonstrate full recovery of the mechanical properties.

for characterization. Tensile tests revealed that the mechanical properties were fully recovered after being remolded for 30 min at 150 °C (Figure 6b). No change was observed in the Young's modulus and stress at break (Figure S10, Supporting Information) while the strain at break ranged between 5.5 and 7.5%, independently of the recycling cycle. In addition, DMA confirmed the recovery of the mechanical properties, as the observed rubbery plateau was constant within experimental error (±5%), which indicates that no cross-links were formed nor broken (Figure 6c). Since we observed a slight shift in the maximum value of tan δ, DSC was performed and showed that the $T_g$ at the second heating changed by less than 1 °C (Figure S12, Supporting Information). In further agreement with DMA, solubility experiments showed that the soluble fraction varied from 7% to 14% without following a clear trend

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(Table S1, Supporting Information), with the soluble fraction of the as-synthesized material being almost identical to that of the material recycled 4 times. Furthermore, no chemical degradation was visible on ATR-FTIR, i.e., the IR-spectra after subsequent cycles are almost identical (Figure S11, Supporting Information). In general, the vinylogous urethane networks exhibited excellent recycling properties over four recycling cycles without loss of mechanical properties or chemical changes.

## 3. Conclusion

In summary, the first catalyst-free vitrimers were developed using the exchange reaction of amines on vinylogous urethanes. These urethane-like chemical moieties emerge as interesting bonds for building polymers, which combine chemical robustness (thermal and hydrolytic stability) with rapid exchange kinetics. Polymer networks were prepared by bulk polymerization of cyclohexane dimethanol bisacetoacetate, *m*-xylylene diamine, and tris(2-aminoethyl)amine. Poly(vinylogous urethane) networks with a glass transition temperature of 87 °C and a storage modulus of ≈2.4 GPa were obtained. As expected for a polymer network, the samples were insoluble even at elevated temperature while a rubbery plateau was observed by DMA. Stress–relaxation and creep experiments showed a viscoelastic liquid behavior. Due to the fast exchange reactions and high density of exchangeable bonds throughout the network, relaxation times as short as 85 s at 170 °C were achieved without the use of any catalyst. Moreover, the poly(vinylogous urethane) networks can be recycled by grinding and without loss of mechanical properties. Since the poly(vinylogous urethane) networks are made from easily accessible chemicals, we expect that a wide range of materials and applications can exploit this new chemistry for vitrimers.

## 4. Experimental Section

*Materials*: 1-Propanol (>99.5%), butylamine (≥99%), benzylamine (≥99%), *m*-xylylene diamine (≥99%), tris(2-aminoethyl)amine (96%), cyclohexane dimethanol (mixture of cis and trans, 99%), 2,2,6-trimethyl-4*H*-1,3-dioxinon-4-one (≥93%), and *tert*-butyl acetoacetate (≥98%) were purchased from Sigma-Aldrich. 2,2,6-Trimethyl-4*H*-1,3-dioxin-4-one was purified by distillation (0.2 Torr, 65–67 °C). The temperature was kept below 90 °C to avoid decomposition.

*Instrumentation*: Nuclear magnetic resonance spectra were recorded on a Bruker Avance 300 or a Bruker Avance II 700 spectrometer at room temperature. IR spectra were collected using a Perkin–Elmer Spectrum1000 FTIR infrared spectrometer with a diamond ATR probe. Thermogravimetric analyses were performed with a Mettler Toledo TGA/SDTA851e instrument under air or nitrogen atmosphere at a heating rate of 10 °C min$^{-1}$ from 25 °C to 500 °C. Differential scanning calorimetry (DSC) analyses were performed with a Mettler Toledo instrument 1/700 under nitrogen atmosphere at a heating rate of 10 °C min$^{-1}$. Dynamic mechanical analysis (DMA) was performed on a SDTA861e DMA from Mettler Toledo. Stress–relaxation experiments were conducted on a Ares G2 rheometer from TA-instruments in torsion geometry with samples of dimension (1.3 × 14.5 × 22 mm$^3$). An axial force of −0.01 N and a deformation of 1% were applied. Creep experiments were performed on rectangular samples (5 mm × 1.4 mm × 10 mm) by using a TA-Q800 DMA; a constant stress of 0.1 MPa was applied. Tensile testing was performed on a Tinius–Olsen H10KT tensile tester, equipped with a 100 N load cell, using a flat dog bone-type specimen with an effective gage length of 13 mm, a width of 2 mm, and a thickness of 1.3 mm. The samples were cut out using a Ray-Ran dog bone cutter. The tensile tests were run at a speed of 10 mm min$^{-1}$.

*Synthetic Procedures (Propyl Acetoacetate)*: 2,2,6-Trimethyl-4*H*-1,3-dioxin-4-one (5.38 g, 34 mM) and 1-propanol (10 mL) were mixed in a pressure tube and heated for 3 h at 135 °C. After the reaction was finished according to thin layer chromatography (TLC), the excess of 1-propanol was removed in vacuo, yielding pure propyl acetoacetate. Yield: 98%, 5.34 g. $^1$H NMR (300 MHz, CDCl$_3$, $\delta$): 4.10 (t, J = 6.5 Hz, 2H), 3.45 (s, 2H), 2.27 (s, 3H), 1.63 (m, 2H), 0.94 (t, J = 6.5 Hz, 3H).

*Propyl-3-(butylamino)but-2-enoate and Propyl-3-(benzylamino)but-2-enoate*: Propyl acetoacetate (0.250 g, 1.73 mM) and butyl- or benzylamine (2 eq, 3.47 mM) were dissolved in 5 mL of methanol and stirred overnight. When the formation of the vinylogous urethane was complete (TLC), the solvent was removed in vacuo and the mixture was extracted twice with brine and CH$_2$Cl$_2$. The combined organic phases were dried with MgSO$_4$ and evaporated, yielding the desired product. The obtained product was purified by flash chromatography using EtOAc/hexane (25/75). Yield of propyl-3-(butylamino)but-2-enoate: 92%, 0,317 g. $^1$H NMR (300 MHz, CDCl$_3$, $\delta$): 8.55 (s, 1H), 4.44 (s, 1H), 3.98 (t, J = 6.77 Hz, 2H), 3.20 (q, J = 6.52 Hz, 2H), 1.91 (s, 3H), 1.65–1.39 (m, 7H), 0.936 (t, J = 7.37 Hz, 6H).

*Yield of Benzyl-3-(butylamino)but-2-enoate*: 94%, 0,379 g. $^1$H NMR (300 MHz, CDCl$_3$, $\delta$): 8.96 (s, 1H), 7.39–7.27 (m, 5H), 4.56 (s, 1H), 4.45 (d, J = 6.36, 2H), 4.02 (t, J = 6.76, 2H), 1.93 (s, 3H), 1.65 (tt, 2H), 0.96 (t, 7,42).

*N-benzyl-3-(benzylamino)but-2-enamide*: A solution of 2,2,6-trimethyl-4*H*-1,3-dioxin-4-one (0.5 g, 3.52 mM) and benzylamine (1.13 g, 10.5 mM) in 1.5 mL of xylene was refluxed for 2 h. When the conversion of the starting product was complete (TLC), the solvent was removed under vacuum. The obtained mixture consisted mainly of *N,N*-benzylacetoacetamide with a small fraction of *N*-benzyl-3-(benzylamine)but-2-enamide, according to $^1$H NMR. This mixture was dissolved in 10 mL of MeOH and benzylamine (0.75 g, 7.04 mM) was added. The mixture was stirred at room temperature over 48 h, resulting in a white suspension. This suspension was poured in 25 mL of water and the white precipitate was filtered off, washed with water, and dried to obtain *N*-benzyl-3-(benzylamino)but-2-enamide. Yield: 85%, 0,83 g. $^1$H NMR (300 MHz, CDCl$_3$, $\delta$): 9.53 (s, 1H), 7.38–7.24 (m, 10H), 4.47–4.39 (m, 5H), 1.89 (s, 3H).

*1,4-Bis(hydroxymethyl)cyclohexane Bis-acetoacetate*: 1,4 cyclohexane dimethanol (88.9 g, 0.61 M) and *tert*-butyl acetoacetate (200 g, 1.26 M) were dissolved in 120 mL of xylene in a 1 L flask equipped with a still head and cooler. The mixture was heated for 90 min at 135 °C. The *tert*-butanol product was removed by distillation during the reaction and the temperature in the still head was typically between 75 and 90 °C. When the temperature dropped to 50 °C, the mixture was cooled and the solvent was removed in vacuo. The resulting crude product crystallized upon cooling with ice and consisted of a 28:72 mixture of the *cis*- and *trans*-isomers, as indicated by the singlets at 4.08 ppm for the *cis*-isomer and 3.97 ppm for the trans-isomer. Recrystallization of the crude product in isopropanol yielded 72% of white crystals, which consisted of 92% of the *trans*-acetoacetate. Yield: 72%, 96.5 g. $^1$H NMR (300 MHz, CDCl$_3$, $\delta$): 4.09 (d, J = 7.19 Hz, 2H cis), 3.97 (d, 6.48 Hz, 2H trans), 3.47 (s, 2H), 2.28 (s, 3H), 1.83–1.78 (m, 4H), 1.68–1.62 (m, 2H), 1.05–1.01 (m, 4H).

*Model Studies*: Benzylamine (0.25 mM, 57 mg) was added to a solution of *N*-butyl vinylogous urethane model compound (0.05 mM, 20 mg) in benzene-d6 (1.5 mL). Five equivalents of benzylamine were used to obtain a pseudo-first order reaction at low conversions. The mixture was heated (100, 120, and 140 °C) in a pressure tube and NMR spectra were taken at different time intervals. The reaction was followed by integration of the two distinct sharp signals at 4.77 ppm and 4.80 pm for the *N*-butyl- and *N*-benzyl model compounds, respectively.

*Network Synthesis*: Xylylene diamine (2.111 g, 15.5 mM), tris(2-aminoethyl)amine (1.774 g, 12.1 mM), and 1,4-cyclohexanedimethanol bisacetoacetate (10 g, 32.0 mM) were mixed in a vial and heated in an oil bath thermostated at 80 °C. When a homogeneous liquid mixture was

obtained, the mixture was taken out of the oil bath while keeping mixing manually. After 2 min, the mixture turned white due to phase separation (water release of the condensation reaction). The resulting white paste was taken out of the vial and pressed into a film of 1.3 mm between two Teflon sheets using a preheated press at 90 °C. After 30 min, the film was transferred into a convection oven and dried during 24 h at 90 °C, followed by a short postcure process of 30 min at 150 °C.

*Solubility Experiments*: Solubility tests were carried out with samples of a size of ($10 \times 10 \times 1.3$ mm$^3$) with a weight of around 170 mg and 25 mL of *N*-methyl-2-pyrrolidone (NMP) as a solvent. The samples were heated for 24 h at 100 °C. Then, the solvent was carefully removed with a syringe and replaced twice by MeOH to remove residual NMP as much as possible. Finally, the samples were dried under vacuum, first overnight at 40 °C and then at 120 °C for 2 h to ensure a complete removal of the solvent from the material. The soluble fraction was calculated using Equation (2); the swelling ratio was calculated using Equation (3)

$$\text{Soluble fraction}(\%) = \frac{m_{\text{initial}} - m_{\text{final}}}{m_{\text{initial}}} \times 100\% \qquad (2)$$

$$\text{Swelling ratio}(\%) = \frac{m_{\text{swollen}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100\% \qquad (3)$$

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

## Acknowledgements

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