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Polymer Chemistry

Vinylogous Urea—Urethane Vitrimers: Accelerating and Inhibiting Network Dynamics through Hydrogen Bonding

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Abstract: Vinylogous urethane (VU_O) based polymer networks are widely used as catalyst-free vitrimers that show rapid covalent bond exchange at elevated temperatures. In solution, vinylogous ureas (VU_N) undergo much faster bond exchange than VU_O and are highly dynamic at room temperature. However, this difference in reactivity is not observed in their respective dynamic polymer networks, as VU_O and VU_N vitrimers prepared herein with very similar macromolecular architectures show comparable stress relaxation and creep behavior. However, by using mixtures of VU_O and VU_N linkages within the same network, the dynamic reactions can be accelerated by an order of magnitude. The results can be rationalized by the effect of intermolecular hydrogen bonding, which is absent in VU_O vitrimers, but is very pronounced for vinylogous urea moieties. At low concentrations of VU_N, these hydrogen bonds act as catalysts for covalent bond exchange, while at high concentration, they provide a pervasive vinylogous urea - urethane (VU) network of strong non-covalent interactions, giving rise to phase separation and inhibiting polymer chain dynamics. This offers a straightforward design principle for dynamic polymer materials, showing at the same time the possible additive and synergistic effects of supramolecular and dynamic covalent polymer networks.

Vinylogous urethanes (VU_O) are strong covalent links, easily derived from amine and acetoacetate building blocks in a straightforward condensation reaction.[1,2] Compared to classical urethane bonds, present in polyurethane (PU) materials, VU_O show a pronounced dynamic covalent bond exchange via *trans*-amination, even in the absence of a catalyst. Owing to their synthetic ease and predictable reactivity, VU_O have been extensively implemented in dynamic covalent networks (DCN)[1,3–9] or networks that have reconfigurable bonds upon a range of stimuli.[10–15] These VU_O polymer networks are also known as "VU" vitrimers, as the VU_O linkages undergo an associative bond exchange, within a permanent polymer network architecture.[16] On account of their overall structural similarity, one would expect VU_O polymer networks to behave similar to conventional PU-based networks. However, this is generally not the case, as VU_O polymer architectures mostly lack phase separation brought on by intermolecular hydrogen bonding.[17] In PUs, the urethane N–H bond is known to coordinate with the carbonyl group of another urethane moiety resulting in the formation of hard segments of associated polymer chains. However, in a VU_O moiety, the N–H bond is prone to internally coordinate to its own carbonyl group in a pseudo-heterocyclic bonding arrangement (Scheme 1).

Thus, VU_O polymers do not readily form hydrogen bonded networks. An alternative dynamic covalent chemistry that does enable intermolecular hydrogen bonding, is offered by vinylogous ureas (VU_N).These are derived from amine and acetoacetamides and thus closely resemble VU_O as they only differ in one skeletal heteroatom (O versus NH).[18] However, VU_N vitrimers have received much less attention than VU_O vitrimers, most likely as VU_N's show rapid covalent bond exchange at room temperature in solution (Figure 1). Thus, polymer networks built up by VU_N linkages would be susceptible to creep, or could otherwise be considered as "too dynamic" for most material applications.[19,20]

Recent works by Rowan,[21–23] Sumerlin,[24] Guan,[25] Konkolewicz,[26] Kalow,[27] among others have demonstrated that bonds with fast exchange dynamics at relatively low temperature can still be leveraged to produce polymer materials with some exceptional characteristics. Motivated by these works, we reinvestigated vinylogous urea - based polymer networks. The obtained networks showed some peculiar, yet promising mechanical and rheological proper-

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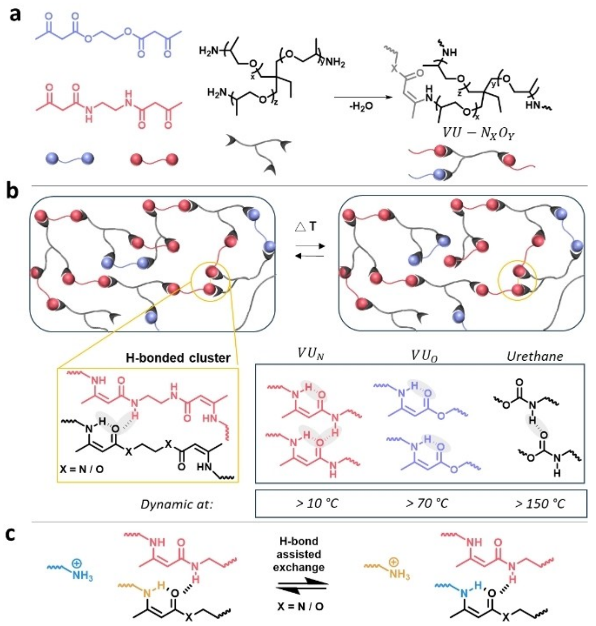

Scheme 1. The material design of the vinylogous urea/urethane networks. (a) The chemical composition of the mixed covalent and supramolecular networks. In blue the *bis*-acetoacetate of ethylene glycol, in red the *bis*-acetoacetamide of ethylenediamine and in black the tri-functional cross-linker with a poly(propylene glycol) backbone. The corresponding network is formed by the condensation of water. (b) Schematic representation of the dynamic network (7/3 urea/urethane) with H-bonded clusters from the urea moieties, restricting the network reconfiguration. Additionally illustrated are the differences in hydrogen bonding in vinylogous ureas (VU_N) (bifurcated), vinylogous urethanes (VU_O) and urethanes with their respective dynamic temperature.[1,18] (c) Catalytic effect of hydrogen bond on the exchange.

ties owing to the interplay of dynamic covalent exchange, hydrogen bonding, and phase separation.

To demonstrate and quantify the significant difference between the exchange rates of VU_O and VU_N dynamic moieties, a revised kinetic study[18] on low molecular weight (MW) model compounds was conducted. To avoid potential influences of proton sources, which could impact the exchange rates, these measurements were carried out using an apolar solvent (benzene), as a mimic for a hydrophobic polymer matrix.[28] The initial *N*-butyl VU_O and VU_N species (**1O** and **1N**, respectively) were readily prepared by the condensation of *N*-butylamine (**BuA**) with the corresponding acetoacetate or acetoacetamide. Model studies were performed whereby **1O** or **1N** was reacted with benzylamine (**BnA**) and subjected to pseudo-first-order conditions in benzene-d_6 at 30 °C and 50 °C, in the absence of a catalyst (Figure 1a). The transamination of **BnA** with **BuA** was followed with ^{1}H NMR spectroscopy as a function of time (Figure S1–S5) for both reagents with the formation of *N*-benzyl vinylogous urea (**1N′**) or *N*-benzyl vinylogous urethane (**1O′**). In agreement with previous studies,[1,18] a rapid increase in the fraction of the transamination product (**1N′**) was observed, whereas little-to-no reaction was observed for **1O** at 50 °C (Figure 1b). The dynamicity of the urea structures is significantly higher at low temperatures compared to urethane structures, which is caused by the earlier reported cationic iminium-pathway that is favoured for the more electron rich vinylogous urea moiety.[18,29]

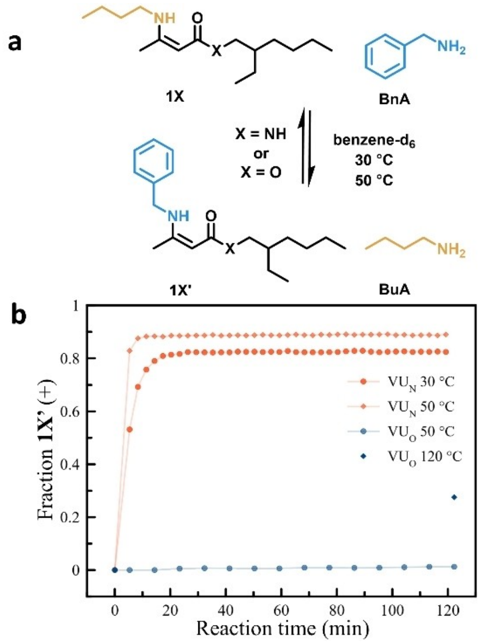

Figure 1. (a) The transamination of the condensation product **1** (formed from acetoacetate (X=O) or acetoacetamide (X=NH) with butylamine **BuA**) with benzylamine **BnA** at elevated temperatures. (b) Decrease of the fraction of butyl model compound **1** through dynamic exchange as a function of time at 30 °C, 50 °C and 120 °C for VUo.

The impact of the room-temperature dynamic urea moieties was next examined at the material level. In this context, a series of vinylogous urea-urethane (VU) networks were prepared using the aforementioned condensation reaction. The *bis*-acetoacetate monomer (forming VU_O) and a *bis*-acetoacetamide monomer (forming VU_N) were mixed with an amine-functionalized polypropoxylated trifunctional crosslinker (Scheme 1a) in *N,N*-dimethylformamide and cast into a Teflon cup to yield a film of the resultant VU networks after drying. The dried films were subsequently compression molded at elevated temperature (130 °C, 15 min, 3kPSI), resulting in robust polymeric films. For consistency with previous work, all materials were prepared with a 5 mol % excess of amines relative to acetoacetates.[1] The resulting macroscopically homogeneous and thermally reprocessable network materials are denoted as $\mathbf{VU{-}N_xO_y}$ in which x and y denote the molar percentages of *bis*-acetoacetamide (**N**) and *bis*-acetoacetate (**O**), respectively, relative to the total 100 %. Preliminary studies demonstrated that the prepared $\mathbf{VU{-}N_xO_y}$ were slightly hygroscopic (Figure S6), and therefore all samples were stored in a desiccator immediately after pressing until analysis.

As an initial approach to evaluate the thermal characteristics of the VU networks, differential scanning calorimetry (DSC) was carried out on all samples. Polymer materials with an increase in mol % in VU_N moieties (from $\mathbf{VU{-}O_{100}}$ to $\mathbf{VU{-}N_{50}O_{50}}$ to $\mathbf{VU{-}N_{100}}$) showed an increase in their glass transition temperatures (T_g) from 7 °C to 34 °C (Fig-

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ure 2a). The T_g increase in the blended networks was found to agree well with the Fox-equation (Figure S7) and can be related to the increase of H-bonding. Interestingly, it was noted that the increase in T_g with increasing VU_N content was accompanied by a peak broadening (breadth of ≈20 °C to ≈40 °C for **VU–O$_{100}$** and **VU–N$_{50}$O$_{50}$**, respectively), as another clear effect of inter-molecular hydrogen bonding on network characteristics. The thermomechanical properties of the networks were investigated rheologically through dynamic temperature ramps (DTR) (Figure 2b). Across all samples, it can be seen that the VU systems are associative in nature as there is no loss of network connectivity at higher temperatures (>100 °C). Despite all networks being formulated with the same crosslink density, the plateau modulus (taken at 120 °C) was found to increase with rising mol % of *bis*-acetoacetamide from **VU–O$_{100}$** to **VU–N$_{100}$**, indicating that an additional non-covalent interaction (H-bonding) is reinforcing the materials, even at high temperatures. The impact of H-bonding is further observed in the corresponding tanδ spectrum. In congruence with the DSC measurements, a rising VU_N concentration was found to result in an increase in T_g with significant and peculiar broadening. For samples with less than 50 % VU_N content, the tanδ behaved as a singular Gaussian peak (Figure 2c). Interestingly, for samples with a content greater than 50 % VU_N, bimodal tanδ spectra were observed (Figure 2d, Figure S14–S15). Upon deconvolution of the tanδ of the enriched urea-materials into two Gaussian peaks, starting from **VU–N$_{60}$O$_{40}$**, it was found that each curve was comprised of a major broad lower temperature peak (interpreted as T_g), followed by a second smaller transition, indicating an additional interaction or phase present in the urea-enriched materials. This second peak, in combination with the increasing G′ modulus in urea-enriched VU networks, suggests that, despite their rapid exchange behavior, VU_N moieties in fact improve the thermomechanical properties of networks through hydrogen bonding. The increased crosslink density and T_g were further verified with tensile tests. When tested under fixed conditions (T_g+30 °C), it was found that modulus and ultimate stress increased with VU_N content, in strong agreement with the rheology data. (Figure S16–S20).

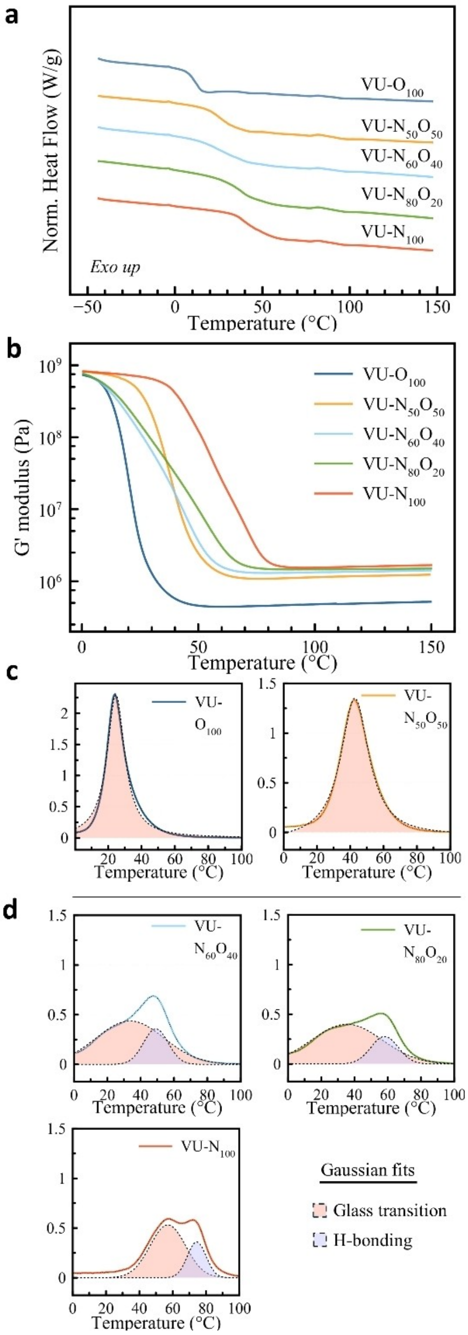

Figure 2. Thermal transitions of the dynamic networks. (a) DSC of the VU-networks at a heating rate of 10 °C/min. (b) DTR of the VU-networks at a heating rate of 3 °C/min. (c) Single tan δ for VU–O100 and VU–N50O50. (d) Deconvolution of the tan δ of VU–N$_{60}$O$_{40}$, VU–N$_{80}$O$_{20}$ and VU–N$_{100}$ as two transitions.

To further support the intriguing results obtained from the thermal data of the VU-materials, additional studies were undertaken to obtain additional confirmation of the suggested supramolecular interactions interplaying in the dynamic networks. Wide-angle X-ray scattering (WAXS) allows for the visualization of material characteristics such as phase separation on a molecular level and the identification of domain sizes based on a correlation function.[20,30] From the two-dimensional WAXS patterns of the two parent networks (**VU–N$_{100}$** and **VU–O$_{100}$**), it can be seen that besides the uniform circular shape, an additional inner contour is present in the 2D pattern for **VU–N$_{100}$**, corresponding with an additional ordered structure in the polymer architecture (Figure 3a). The one-dimensional WAXS (Figure 3b) clearly shows this feature at $q \approx 0.3$ Å^{-1} as an additional diffraction peak for all samples except for **VU–O$_{100}$** (lacking intermolecular hydrogen bonds). The spacing can be estimated at 1.8–2 nm, which might be attributed to hydrogen bond-induced clustering.[31] It is also noteworthy that additional tailing at $q \approx 0.95$ Å^{-1} (0.65 nm) appears next to the amorphous polymer structure ($q \approx 1.36$ Å^{-1}, 0.46 nm) with increasing urea content (**VU–O$_{100}$** vs **VU–N$_{100}$**). Hydrogen-bonded domains can thus be envisioned, resulting in a percolated polymer network

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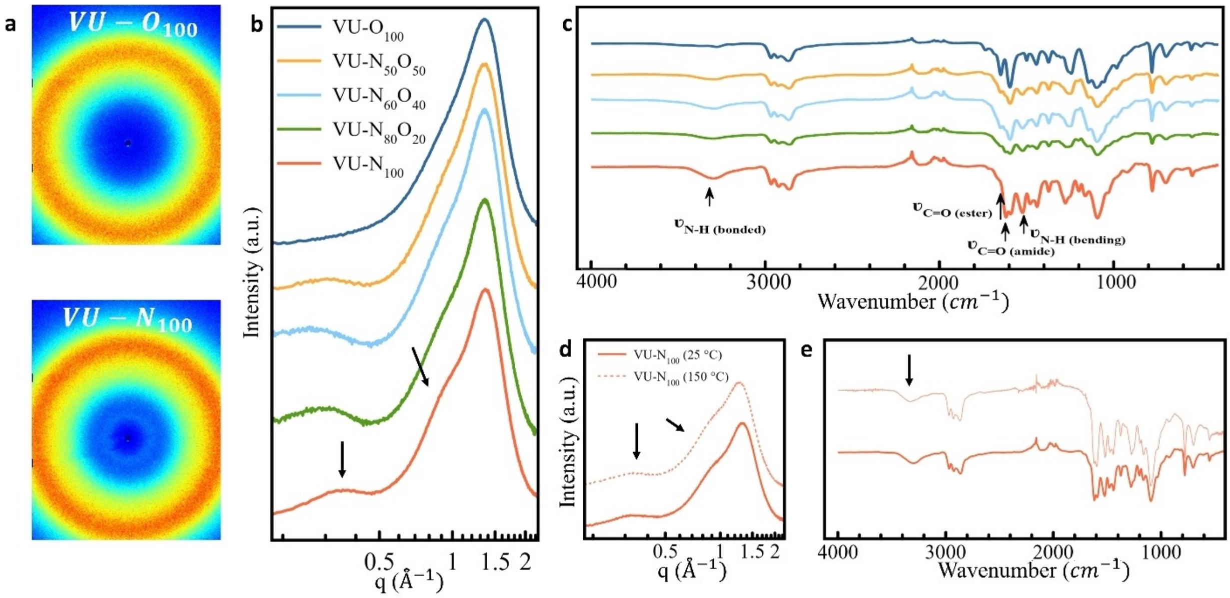

Figure 3. (a) Two-dimensional Wide-Angle X-Ray Scattering (WAXS) patterns for VU–O_{100} and VU–N_{100}. (b) One-dimensional WAXS measured for all VU-materials. (c) Fourier-Transform Infrared (FTIR) spectroscopy of all materials. (d) WAXS of VU–N_{100} at 25 °C (full line) and at 150 °C (dashed line). (e) FTIR of VU–N_{100} at 25 °C (dark red line) and at 150 °C (light red line).

(when $>50\,\%$ VU_N), which is in agreement with the previously observed thermomechanical data.

From the FTIR spectrum (Figure 3c, Figure S23), it can be concluded that all materials are well cured as can be evidenced by almost full disappearance of the strong C=O ketone absorptions at 1730 and 1710 cm^{-1}. More interestingly, a broad band at 3320 cm^{-1} can be observed starting from the **VU–$N_{50}O_{50}$**, which is attributed to the hydrogen-bonded N–H stretches in the VU-matrix, as opposed to non-hydrogen-bonded N–H stretches which would appear at 3480 cm^{-1}.[32] In addition, the urea-based materials contain a C=O stretch of the amide at 1618 cm^{-1} while this cannot be visualised for the **VU–O_{100}** materials. Hydrogen-bonded supramolecular polymers are often considered to be quite dynamic with temperature,[33] however, even at elevated temperatures (150 °C), the associated signature peaks were maintained in both WAXS and FTIR ($q \approx 0.3$ Å^{-1} and $\upsilon = 3320$ cm^{-1} in Figures 3d and 3e, respectively). This suggests the formation of durable hydrogen bonding between polymer chains, limiting the motion of the polymer strands that are associatively exchanging and resulting eventually in a percolated dynamic network.

With an understanding of the microscopic detail in hand, the stress relaxation and creep performance of the materials could be evaluated. In agreement with the slow rate of exchange highlighted by small molecule kinetics, the stress-relaxation data at 150 °C shows that the urethane material (**VU–O_{100}**) relaxes the slowest ($\tau^* \approx 239$ s, Figures 4a and 4b). Surprisingly, the exclusive vinylogous urea network (**VU–N_{100}**) did not show a significant difference in relaxation, which is in stark contrast with the expectation from the small molecule kinetics. In fact, the two stress relaxation curves and relaxation times are quite comparable. Interestingly, the "mixed" networks do show a significant effect in their stress relaxation behaviour, and all of them are more dynamic than the parent polymer networks. The most dynamic material, **VU–$N_{90}O_{10}$** shows a stress-relaxation time at 150 °C that is an order of magnitude faster ($\tau^* \approx 12$ s). This peculiar behaviour can be ascribed to the effect of hydrogen bonding. A high amount of hydrogen bonding is apparently inhibiting the associative exchange as strong non-covalent H-bonds must be broken first[34] (Scheme 1), whereas a smaller amount of hydrogen bonds can act as a catalyst for the covalent dynamic bond exchange reactions. It should be noted (Figure S32) that the activation energies of most networks are comparable while their relaxation times are not, which is indicative of a catalytic effect of the hydrogen bonds (i.e. pre-exponential factor).[28]

The observed accelerating-inhibiting behaviour can be attractive for the design of creep-resistant materials. A control over creep can indeed be enforced by introducing hydrogen bonds, rather than only considering the dynamic exchange of the respective dynamic chemistries. Thus, creep measurements were taken in a temperature window of 50–110 °C. Also here, the same trend as for the stress relaxation is shown in the creep data, as the slope of the **VU–$N_{50}O_{50}$** is steeper compared to **VU–N_{100}** and **VU–O_{100}** at 90 °C. While in solution the vinylogous urea groups exchanged much faster at 50 °C compared to the vinylogous urethanes (Figure 1b), there is almost no difference in creep rate at the material level (Figure S36), which is in agreement with the aforementioned data and confirms that strong hydrogen bonding was able to reduce the degree of creep.

CONCLUSION: The research results reported herein highlight a few important aspects that are not generally considered in the design of covalent dynamic polymer networks. First of all, highly reactive room-temperature dynamic covalent bonds can be used in the design of soft

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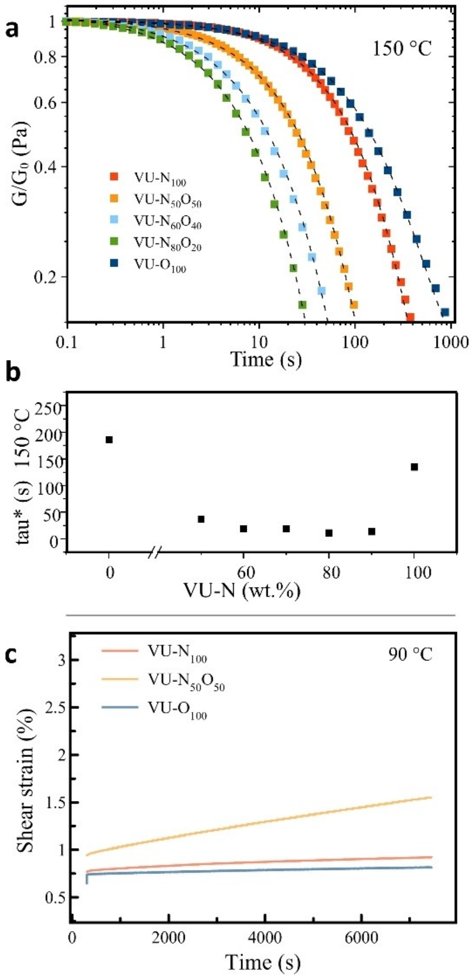

Figure 4. (a) Normalized stress-relaxation curves at 150 °C for the VU-materials. (b) Apparent stress relaxation time tau* at 150 °C plotted as a function of wt.% VU–N. (c) Shear strain as a function of time for the VU-materials at 90 °C for an applied stress of 4000 Pa.

materials with low creep, when combined with hydrogen bonds. Secondly, the interplay of covalent and non-covalent interactions can be complex, as shown by the dual effect of hydrogen bonding in VU$_N$-networks, acting both as an inhibitor of network relaxation through non-covalent interaction and as a catalyst of bond exchange reactions, by forming hydrogen bonds that increase the electrophilicity of the vinylogous urea bonds. The fine-tuning of dynamic covalent networks by combining them with dynamic non-covalent networks (i.e. supramolecular networks) is thus expected to become a powerful design strategy. Lastly, our findings also highlight the fact that exchange reactions that are deemed to be too fast, can still be used in the design of creep resistant dynamic polymer networks, by attenuating their reactivity with supramolecular constraints.

Supporting Information

Monomer and material synthesis and network characterization (rheology, tensile tests, etc.) (PDF).

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Hydrogen-Bonding · Vinylogous Urea-Urethane · Vitrimers

[1] W. Denissen, G. Rivero, R. Nicolaÿ, L. Leibler, J. M. Winne, F. E. Du Prez, *Adv. Funct. Mater.* **2015**, *25*, 2451–2457.
[2] Y. Spiesschaert, M. Guerre, I. De Baere, W. Van Paepegem, J. M. Winne, F. E. Du Prez, *Macromolecules* **2020**, *53*, 2485–2495.
[3] J. S. A. Ishibashi, I. C. Pierce, A. B. Chang, A. Zografos, B. M. El-Zaatari, Y. Fang, S. J. Weigand, F. S. Bates, J. A. Kalow, *Macromolecules* **2021**, *54*, 3972–3986.
[4] P. Haida, S. Chirachanchai, V. Abetz, *ACS Sustainable Chem. Eng.* **2023**, *11*, 8350–8361.
[5] S. Engelen, A. A. Wroblewska, K. De Bruycker, R. Aksakal, V. Ladmiral, S. Caillol, F. E. Du Prez, *Polym. Chem.* **2022**, *13*, 2665–2673.
[6] J. O. Holloway, C. Taplan, F. E. Du Prez, *Polym. Chem.* **2022**, *13*, 2008–2018.
[7] Y. Zhu, F. Gao, J. Zhong, L. Shen, Y. Lin, *Eur. Polym. J.* **2020**, *135*, 109865.
[8] P. Haida, V. Abetz, *Macromol. Rapid Commun.* **2020**, *41*, 2000273.

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[9] P. Haida, G. Signorato, V. Abetz, *Polym. Chem.* **2022**, *13*, 946–958.

[10] S. J. Rowan, S. J. Cantrill, G. R. L. Cousins, J. K. M. Sanders, J. F. Stoddart, *Angew. Chem. Int. Ed.* **2002**, *41*, 898–952.

[11] C. J. Kloxin, C. N. Bowman, *Chem. Soc. Rev.* **2013**, *42*, 7161–7173.

[12] J. M. Winne, L. Leibler, F. E. Du Prez, *Polym. Chem.* **2019**, *10*, 6091–6108.

[13] R. J. Wojtecki, M. A. Meador, S. J. Rowan, *Nat. Mater.* **2011**, *10*, 14–27.

[14] N. Zheng, Y. Xu, Q. Zhao, T. Xie, *Chem. Rev.* **2021**, *121*, 1716–1745.

[15] Y. Mao, Y. Kubota, R. Feng, J. Gong, A. Ishigami, Y. Kobayashi, T. Watabe, D. Aoki, H. Otsuka, H. Ito, *Macromolecules* **2022**, *55*, 3948–3957.

[16] W. Denissen, J. M. Winne, F. E. Du Prez, *Chem. Sci.* **2016**, *7*, 30–38.

[17] R. Bonart, E. H. Muller, *J. Macromol. Sci. Part B* **1974**, *10*, 177–189.

[18] W. Denissen, I. De Baere, W. Van Paepegem, L. Leibler, J. Winne, F. E. Du Prez, *Macromolecules* **2018**, *51*, 2054–2064.

[19] F. Van Lijsebetten, T. Debsharma, M. J. Winne, F. E. Du Prez, *Angew. Chem. Int. Ed.* **2022**, *61*, e202210405.

[20] M. H. P. de Heer Kloots, S. K. Schoustra, J. A. Dijksman, M. M. J. Smulders, *Soft Matter* **2023**, *19*, 2857–2877.

[21] K. M. Herbert, P. T. Getty, N. D. Dolinski, J. E. Hertzog, D. De Jong, J. H. Lettow, J. Romulus, J. W. Onorato, E. M. Foster, S. J. Rowan, *Chem. Sci.* **2020**, *11*, 5028–5036.

[22] K. M. Herbert, N. D. Dolinski, N. R. Boynton, J. G. Murphy, C. A. Lindberg, S. J. Sibener, S. J. Rowan, *ACS Appl. Mater. Interfaces* **2021**, *13*, 27471–27480.

[23] A. E. Crolais, N. D. Dolinski, N. R. Boynton, J. M. Radhakrishnan, S. A. Snyder, S. J. Rowan, *J. Am. Chem. Soc.* **2023**, *145*, 14427–14434.

[24] J. J. Cash, T. Kubo, A. P. Bapat, B. S. Sumerlin, *Macromolecules* **2015**, *48*, 2098–2106.

[25] O. R. Cromwell, J. Chung, Z. Guan, *J. Am. Chem. Soc.* **2015**, *137*, 6492–6495.

[26] N. De Alwis Watuthanthrige, D. Dunn, M. Dolan, J. L. Sparks, Z. Ye, M. B. Zanjani, D. Konkolewicz, *ACS Appl. Polym. Mater.* **2022**, *4*, 1475–1486.

[27] B. Kang, J. A. Kalow, *ACS Macro Lett.* **2022**, *11*, 394–401.

[28] W. Denissen, M. Droesbeke, R. Nicolay, L. Leibler, J. M. Winne, F. E. Du Prez, *Nat. Commun.* **2017**, *8*, 14857.

[29] M. Guerre, C. Taplan, R. Nicolaÿ, J. M. Winne, F. E. Du Prez, *J. Am. Chem. Soc.* **2018**, *140*, 13272–13284.

[30] R. G. Ricarte, F. Tournilhac, L. Leibler, *Macromolecules* **2019**, *52*, 432–443.

[31] W. P. J. Appel, G. Portale, E. Wisse, P. Y. W. Dankers, E. W. Meijer, *Macromolecules* **2011**, *44*, 6776–6784.

[32] Y. I. Tien, K. H. Wei, *Polymer* **2001**, *42*, 3213–3221.

[33] K. Yamauchi, J. R. Lizotte, T. E. Long, *Macromolecules* **2003**, *36*, 1083–1088.

[34] C. Zhang, Z. Yang, N. T. Duong, X. Li, Y. Nishiyama, Q. Wu, R. Zhang, P. Sun, *Macromolecules* **2019**, *52*, 5014–5025.

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Communications

Polymer Chemistry

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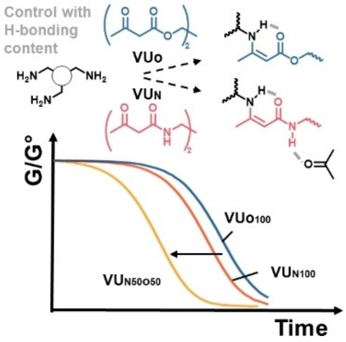
Vinylogous Urea—Urethane Vitrimers: Accelerating and Inhibiting Network Dynamics through Hydrogen Bonding



In solution, vinylogous urea (VU$_N$) groups undergo much faster bond exchange than vinylogous urethanes (VU$_O$), but this is not observed in their respective polymer networks. Surprisingly, blends of the two monomer types show increased network dynamics. The effects are correlated to hydrogen bonding, which catalyses covalent exchange and also reinforces networks by non-covalent interactions.

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