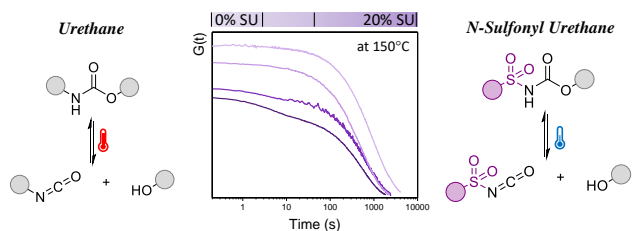


N-Sulfonyl-urethanes to Design Polyurethane Networks with Temperature-Controlled Dynamicity

Stephan Maes, Filip Van Lijsebetten, Johan M. Winne* and Filip E. Du Prez*

Polymer Chemistry Research group, Centre of Macromolecular Chemistry (CMaC) and Laboratory of Organic Synthesis, Department of Organic and Macromolecular Chemistry, Faculty of Sciences, Ghent University, Krijgslaan 281-S4, Ghent, 9000, Belgium.

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ABSTRACT

(Re-)processing of cross-linked polyurethanes (PUs) is often energy intensive and inefficient since dissociation of urethane linkages at elevated temperatures generates highly reactive isocyanate moieties that can react with a wide range of nucleophiles. In this study, we first show with a small molecule study that the introduction of N-sulfonyl urethane bonds leads to dynamic covalent exchange reactions under much milder conditions compared to regular urethane groups. Then, these exchangeable N-sulfonyl urethane motifs have been introduced, in relatively small amounts

(5, 10 and 20%), in a cross-linked PU-matrix in an attempt to facilitate plastic flow at lower temperatures. Rheological analysis of the elastomeric dissociative networks revealed an interesting double relaxation behavior, even for temperatures between 150 and 100 °C, which could be described by a Maxwell model with two elements, which can be related to the activated and less activated urethane bonds. Finally, the (re-)processability of these sulfonyl urethane containing PUs was demonstrated through multiple cutting and hot pressing cycles and the corresponding materials showed a good retention of thermal properties.

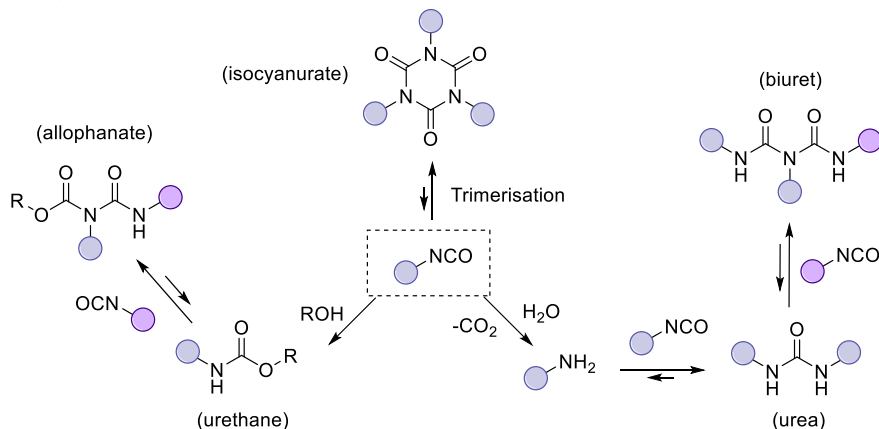
INTRODUCTION

Polyurethanes (PUs) are one of the most common cross-linked bulk polymers used in a wide range of applications, from foams to coatings, owing to the ability of simple precursors (*i.e.* isocyanates and polyols) to produce both flexible and rigid end products.^{1,2} However, reprocessing or remolding conventionally cross-linked PUs is time-consuming and inefficient, currently preventing the recycling of PU waste on large scale. Because PUs account for roughly 30% of the thermoset market, novel methods of repurposing or recycling are highly sought after in academia and industry. One popular approach to impart plastic flow and processability into various types of infusible thermosets has been to introduce reversible bonds that respond to a specific trigger (*e.g.* temperature). The resulting materials, known as covalent adaptable networks (CANs) or dynamic covalent polymer networks (DCPNs), should ideally be able to withstand deformation during use while still flowing significantly after activation (*e.g.* at high temperatures).³⁻⁷ As a result, a wide array of dynamic chemistries have been introduced to common thermoset matrices including furan-maleimides,⁸⁻¹⁰ imines,^{11,12} transesterification,¹³⁻¹⁵ disulfides,^{16,17} and boron-based

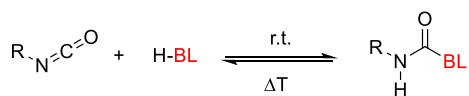
chemistries.¹⁸⁻²⁰ Moreover, all of the aforementioned chemistries have been introduced into a PU matrix.²¹

Importantly, whereas other thermosets, such as epoxies and polyesters, are typically formed by making use of irreversible bonds, PUs are intrinsically different polymer matrices, as they show an inherent bond exchange reactivity. Indeed, the reversibility of urethane linkages is well known to occur around 180 °C (even in the absence of catalysts), which can be attributed primarily to the relative facile reformation of isocyanates, that can then swiftly recombine with other nucleophiles.²²⁻²⁵ However, because the regenerated isocyanate is susceptible to re-cross-linking with virtually any nucleophilic active hydrogen compound within a polymer matrix (including absorbed moisture), thermally reprocessing regular PU materials is difficult to control. For the reformation of bonds to the isocyanate, multiple reactions compete, producing urethane, urea, allophanate, biuret and isocyanurate structures, each having their own varying degrees of reversibility as dynamic or less dynamic linkages (**Scheme 1 a**). Nonetheless, while this wide set of possible competing reactions contribute to the wide range of applications that can be targeted with PU materials, it also complicates the introduction of more controlled reactive cross-linking chemistries inside this chemically somewhat intractable, or at least highly convoluted matrix. Given the recent surge in interest in dynamic covalent chemistry within the polymer sciences, there has also been renewed interest in the study and control of the intrinsic PU dynamicity.

a) Isocyanate reactivity

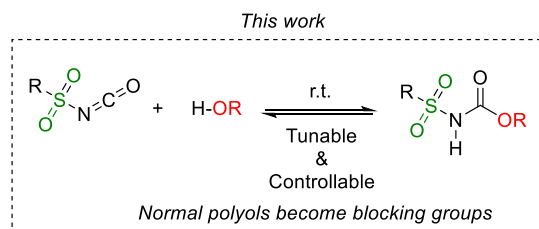


b) Blocked isocyanates



Traditional BL = oximes, caprolactams, pyrazoles...

"Covalent adaptable" BL = acylsemicarbazide, hindered amines, thiols, alcohols...



Scheme 1. a) Schematic representation of common reaction products observed in polyurethane materials. b) Blocked isocyanates as inspiration for the development of blocked sulfonyl isocyanates.

While numerous alternative strategies exist,^{26–28} blocked isocyanates have proven to be one of the most successful approaches for a more temperature-controlled reactivity, as evidenced by the large number of patent applications on the subject (**Scheme 1 b**).^{29,30} Importantly, the rate and extent of reversion of the blocked adduct will be affected by a variety of factors, including the nature of the blocking agent and isocyanate, the presence of a catalyst, and temperature. Classic examples of blocking agents are oximes,^{31,32} caprolactams,³³ acylsemicarbazide,³⁴ or pyrazoles,³⁵ which deliver bench-stable monomers but are more difficult to apply in polymer networks. In contrast, several research groups recently demonstrated that, with appropriate catalysis, much more common

compounds such as aliphatic thiols can be used to temporarily regenerate isocyanates and create (re-)processable polythiourethanes.^{36–38}

Motivated by the promising results obtained with thiourethanes, Hillmyer, Dichtel, Xie, and others revisited the dynamicity of regular urethane linkages in which the constituting polyol (*e.g.* with a polyester, polyether or fatty acid backbone) could be regarded as a formal blocking agent.^{39–45} However, as demonstrated by Torkelson and co-workers, complete recovery of the original urethane cross-links is impossible without the use of specific catalysts and/or an excess of alcohols.^{46,47} Furthermore, even in these cases, it is difficult to rule out the formation of other (more stable) structures such as ureas, allophanates, and biurets during thermomechanical recycling. Thus, an important research question for the (re-)processability of PU-networks (and the controlled (re)generation of isocyanates within those matrices) is how the equilibrium distribution can be directed, and how this affects the final thermomechanical properties of the recycled product.

Changing the steric and electronic environment surrounding a dynamic covalent bond is arguably one of the simplest ways to modify reactivity and steer the outcome. Indeed, several research groups, including our own, have recently demonstrated that the addition of electron-withdrawing and electron-donating groups has a significant impact on the thermodynamics ($K_{eq}[T] \sim G[T]$) and kinetics of bond exchange ($\nu_{ex}[T] \sim \tau[T]$) in vitrimers and dissociative CANs.^{48–53} More specifically, by making intermediates more reactive and thus shorter-lived, fast material flow at lower temperatures (*e.g.* 140–160 °C) can be achieved, limiting the possibility of side-reactions.⁵⁴ Given these findings, one appealing strategy for PUs would be to attach an electron-withdrawing group to an isocyanate, increasing the overall dynamicity of the resulting urethane cross-linkage and PU network.

Sulfonyl isocyanates are a relatively unexplored class of modified isocyanates that are known in organic synthesis to be efficient coupling reagents for the production of N-sulfonyl urethanes (SUs), even with hindered alcohols.⁵⁵⁻⁵⁷ Because of the electron-withdrawing effect of the sulfonyl moiety, SUs can be thought of as reversibly blocked isocyanates that can simultaneously add acidity to PU materials.⁵⁸⁻⁶⁰ The sulfonyl urethane *NH* proton is indeed quite acidic, and with a pKa value around 3.5, it is frequently compared to carboxylic acids.⁶¹⁻⁶³ As a result, we hypothesized that adding a specific amount of SU-moieties in a cross-linked matrix would not only introduce an internal acid catalyst but would also help to improve controlled (de)cross-linking of PU materials.^{64,65} In fact, our own research group demonstrated several times how blocked or delayed (very reactive) systems can be engineered to produce polymeric materials with customized dynamic properties.⁶⁶⁻⁶⁹

Herein, we report a strategy to introduce SU-motifs as blocked isocyanates to promote and control the thermomechanical recycling of PU materials at lower temperatures. Specifically, SUs with multiple functionalities were added as co-monomers to regular PU formulations to obtain cross-linked polymer networks with varying degrees of built-in acidic SU units. First, small molecule studies were performed to investigate the efficient blocking and deblocking of SUs to the corresponding sulfonyl isocyanate and alcohol moiety. Following that, rheology experiments at the material level were carried out to gain mechanistic insights into the way how the introduction of “masked” sulfonyl isocyanates would affect (re)processability. Furthermore, the obtained polymer networks were subjected to extensive mechanical, thermal, solubility, and recycling tests in order to obtain more “molecular information” about isocyanate-based dynamic chemistries in general.

RESULTS AND DISCUSSION

Synthesis and evaluation of blocked sulfonyl isocyanates

A first objective of this work was to determine the onset of reversibility or deblocking temperature of the SU adducts. Interestingly, previous studies already indicated that heating the SUs in the presence of an alcohol or amine, results in the thermal deprotection of the sulfonyl isocyanate and swift conversion to the exchange product.⁵⁸⁻⁶⁰ However, information regarding the kinetics and extent of SU reversion at a given temperature is lacking. To that end, several model compounds were prepared by adding commercially available *para*-toluenesulfonyl isocyanate (*p*-TsNCO) to a cooled solution of a selection of alcohols. Reactions with methanol (**SU-Me, 1**), decanol (**SU-De, 2**) and triethylene glycol monoethyl ether (**SU-TEG, 3**) proceeded swiftly to give the corresponding SUs in quantitative yields within minutes. The chosen alcohols were used specifically to have a low boiling, high boiling, and polar blocking agent, respectively (*vide infra* for rationale). Besides these model compounds, a regular urethane (decyl N-phenyl carbamate, **4**) was synthesized and used as a benchmark.

Initial assessment of the sulfonyl isocyanate deblocking parameters was done *via* DSC and TGA analysis of **1**, **2**, **3** and **4**. Large endothermic melting peaks are observed at 64, 72 and 112°C for **4**, **2** and **1** respectively (**Figure 1 b** and **Figure S1**). Model compound **3** does not have an endothermic peak **Figure 1 b**, while **Figure S1** reveals a phase transition around -38°C. Interestingly, while an endothermic peak is still observed for **4** in the second heating (**Figure 1 b**), no clear signal is visible for **1** and **2**, which is a first indication of the less favorable dissociation of **4**. TGA revealed a 5% weight loss starting around 200°C and complete decomposition at 250°C for all compounds, with the greatest stability for SU-TEG (**Figure 1 c**).

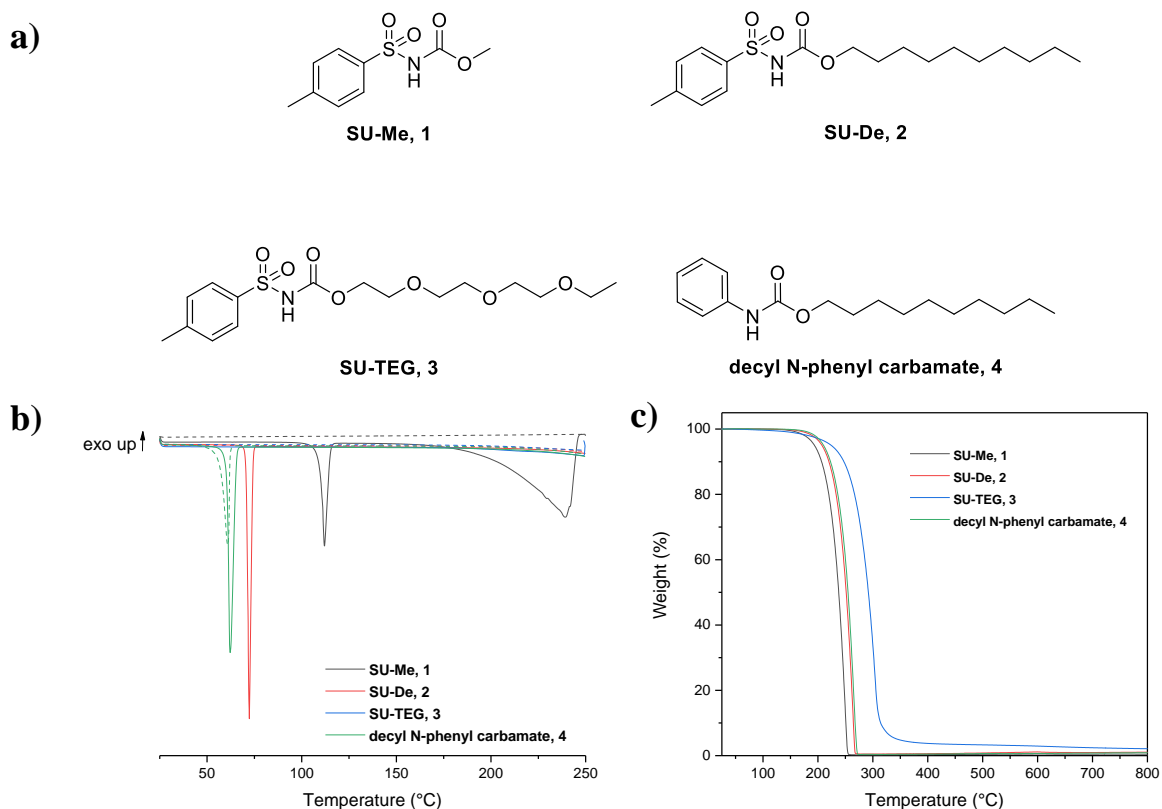


Figure 1. a) Structures of the model sulfonyl urethane components SU-Me (1), SU-De (2), SU-TEG (3) and decyl N-phenyl carbamate (4). b) DSC thermograms of **1**, **2**, **3** and **4** measured at $5^{\circ}\text{C min}^{-1}$ under N_2 atmosphere (-: first heating curve; -: second heating curve). c) TGA thermogram of **1**, **2**, **3** and **4** measured at a heating rate of $10^{\circ}\text{C min}^{-1}$.

Subsequently, the kinetics of deblocking were investigated using offline $^1\text{H-NMR}$ analysis to monitor the formation of an exchange product when heating SU-De for 60 minutes in the presence of excess benzyl alcohol (**Figure 2**). Hence, the fraction of released sulfonyl isocyanate could be conveniently monitored in an interval between 80 and 130°C (**Figure S2-7** and **Table S1**), which allowed to determine rate constants k_{obs} for each investigated temperature by fitting the experimental data to the rate equation of sulfonyl urethane consumption (**Eq S1-3**). Moreover, plotting $\ln(k_{obs})$ against $1000/T$ in an Arrhenius plot, allowed to determine an apparent activation

energy ($E_{a,ex}$) of $77.1 \pm 4.62 \text{ kJ mol}^{-1}$ from the slope of the curve, which was in the same order of magnitude as previously reported dynamic systems.⁵⁰ In line with our previous investigations regarding thermal deblocking systems,^{68,69} we could also identify an initial “deblocking temperature” at $\sim 90 \text{ }^\circ\text{C}$ (point at which 5% of adduct is released after 15 min) and a “half-life temperature” at $\sim 130 \text{ }^\circ\text{C}$ (point at which 50% of adduct is released after 15 min) to identify at which temperature sulfonyl isocyanate release became relatively fast. In contrast, when performing the same experiment with decyl N-phenyl carbamate (**4**) at $100 \text{ }^\circ\text{C}$ (*i.e.* above the deblocking temperature of SU-De), no exchange products could be determined (**Figure S8**).

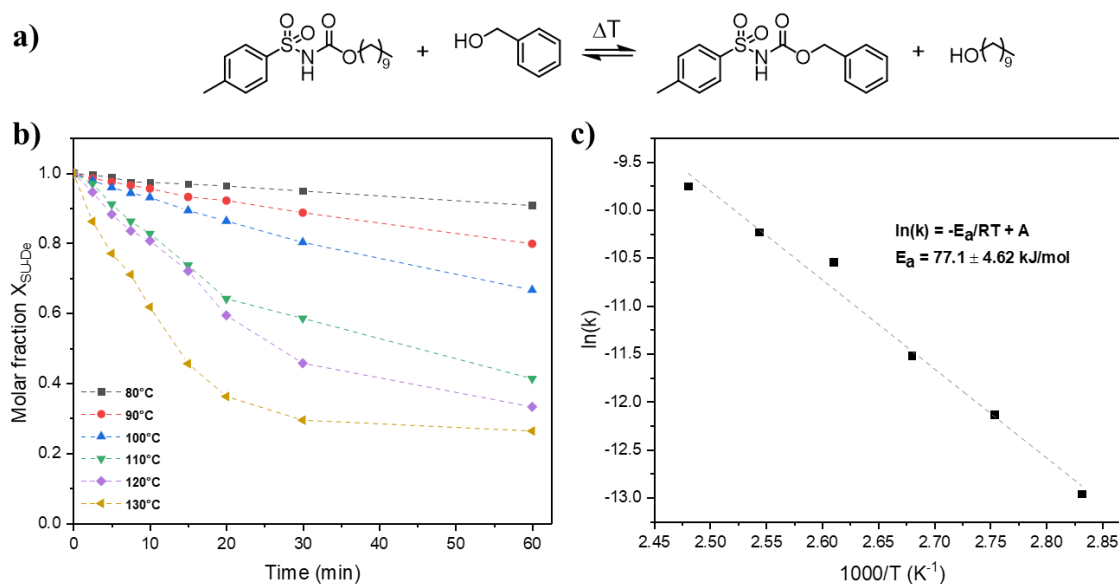


Figure 2. a) Exchange reaction between SU-De and benzyl alcohol. b) Plot of the molar fraction of SU-De as a function of time and c) related Arrhenius plot.

As expected, the stoichiometric excess of benzyl alcohol impacted the reaction rate (**Figure S9-12** and **Table S2**). Based on these experiments, a purely associative exchange mechanism cannot unambiguously be confirmed. Indeed, in line with common urethanes, a dissociative exchange

behavior - yielding sulfonyl isocyanates and alcohols as intermediates - could not be excluded. In order to investigate the possibility of such a dissociative exchange pathway, two different sulfonyl urethanes were mixed and heated in a crossover experiment, after which LC-MS analysis showed the presence of starting as well as exchange products (**Figure S13**). Based on the kinetics as well as the crossover experiments, it can be concluded that both associative and dissociative exchange is possible depending on the environmental conditions *i.e.* whether or not free hydroxyl groups are available. Interestingly, this dissociative pathway does not require the presence of hydrophilic hydroxyl groups, which is in turn protecting the SU bonds from hydrolysis, indicating that the isocyanates are relatively stable, and recombine cleanly even with the generated low amount of free hydroxyls.

When introducing the acidic SU groups into PU materials, a valid concern could indeed be related to the hydrolysis resistance of these blocked sulfonyl isocyanate adducts. Naturally, this heavily depends on the environmental conditions and whether hydrolysis sensitive sulfonyl isocyanates are prematurely released during the process. To that end, SU-TEG was used as a hydrophilic model compound that could be completely dissolved in deuterated water, allowing to track SU decomposition by recording ¹H-NMR spectra at regular time intervals. It could be concluded that temperature had a significant effect on small molecule level, with limited hydrolysis at 25 °C over 40 days and complete decomposition at 80 °C after 5 hours, which could be explained by the fact that this was close to the deblocking temperature as described above (**Figures S14-17** and **Tables S3-5**).

Blocked sulfonyl isocyanates in polyurethane networks

Starting from the aforementioned qualitative insights into the dynamic behavior of blocked sulfonyl isocyanates, some rational material design rules could be drawn. As SU moieties are highly polar structures with strong hydrogen bonding capacity, they can attract water over time. Therefore, the amount of SU motifs in the PU material should be controlled to retain the polarity of the polymer matrix and have a good balance between reactivity and stability. To that end, a set of PU networks was prepared with a variable amount of SU bonds up to 20 mol%. First, a benchmark PU was synthesized by equimolar mixing of the bifunctional alcohol Pripol 2033 (**5**) and trifunctional isocyanate Desmodur N3600 (**6**) with 1 mol% dibutyl tin dilaurate (DBTDL) catalyst (**PUSU-0**, *i.e.* 0% of SU bonds present in the material). As bifunctional sulfonyl isocyanates are neither commercially available, nor bench stable, a blocked bifunctional sulfonyl isocyanate monomer (**7**) was prepared from 1,3-benzene disulfonyl chloride in a straightforward fashion (see Supporting Information). Modified PUs were then made by adding **7** as co-monomer to a large excess of diol **5** at 140 °C for 1 h to generate sulfonyl urethane moieties embedded in dynamic chain extenders/curing agent (**Figure S18** for NMR spectrum) and further curing through reaction of all hydroxyl groups with trifunctional isocyanate **6** (**Figure 3**). As a result, materials with a similar composition to PUSU-0 could be obtained (*i.e.* consisting of mainly diol **5** and trifunctional isocyanate **6**), when adjusting the amount of diol **5** to take into account the incorporation of 5, 10 or 20 mol % of SU units prior to network formation at 80 °C for 16 h. The resulting materials, further referred to as **PUSU-5**, **PUSU-10** and **PUSU-20**, were analyzed *via* ATR-FTIR to monitor the disappearance of the isocyanate peak at 2270 cm⁻¹ (**Figure S19**).

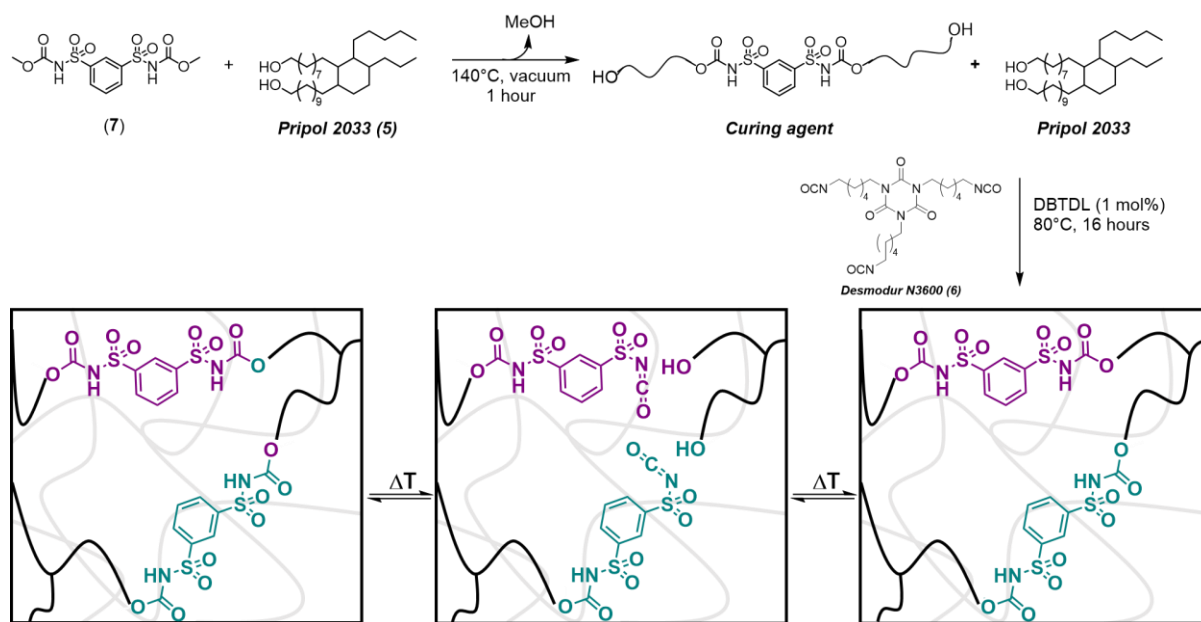


Figure 3. General reaction scheme for the synthesis of sulfonyl urethane diol curing agent from 7 and Pripol 2033 (5). Addition of Desmodur N3600 (6) and a catalytic amount of DBTDL yields a sulfonyl urethane containing material.

The (re)processability of all of the aforementioned (modified) networks was initially investigated using compression molding. Homogeneous samples of PUSU-5 to PUSU-20 could be obtained after shredding the pristine materials and heating for 1 h at 140 °C while applying a pressure of 2 tons. Interestingly, even after 3 h of applying the same conditions to PUSU-0, no well-consolidated samples could be obtained, in line with the previously mentioned need for specific catalysts and high temperature to (re)process conventional PU materials (**Figure S20**). From differential scanning calorimetry (DSC) analysis (**Figure S21**), glass transition temperature (T_g) values were obtained in the range of -4 to 0 °C, indicating the formation of flexible PUs (see **Table 1**). These values were in good agreement with the glass transition temperatures obtained from DMTA measurements (6.1, 8.8 and 4.3 °C for PUSU-5, PUSU-10 and PUSU-20 respectively). Interestingly, the DMTA-thermogram of PUSU-20 shows a clear second transition around -17.6

°C, which might (to some extent) be attributed to thermally reversible phase separation (**Figure S22**). Because of the large Pripol 2033 content, high thermal stability could be observed after TGA analysis with $T_{\text{deg},5\%}$ around 320 °C (**Figure S23**). Isothermal TGA measurements at 140 °C for 80 min further confirmed negligible mass losses at (re)processing conditions (**Figure S24**). Moreover, only minor mass losses (1.2%) are observed for PUSU-20 at 150°C for 12 h (**Figure S25**).

Table 1. Overview of the thermal and mechanical properties of the N-sulfonyl urethane containing polyurethanes.

Properties	PUSU-0	PUSU-5	PUSU-10	PUSU-20
T_g (°C) ^(a)	0	-2	-4	-4
$T_{\text{deg},5\%}$ (°C) ^(b)	323	318	324	312
Swelling ratio (%) ^(c)	133 ± 4	151 ± 2	113 ± 1	159 ± 6
Soluble fraction (%) ^(c)	1 ± 1	3 ± 2	1 ± 0.5	6 ± 4
E-modulus (MPa) ^(d)	n.d. ^(e)	2.14 ± 0.24	2.44 ± 0.46	4.17 ± 0.56
Strain at break (%) ^(d)	n.d. ^(e)	124.12 ± 27.60	199.98 ± 59.79	237.14 ± 63.64
Stress at break (MPa) ^(d)	n.d. ^(e)	1.64 ± 0.26	2.83 ± 0.97	4.78 ± 1.63

^a Obtained from the second heating curve of DSC measurements with heating and cooling rate of 10 K min⁻¹. ^b Determined as onset temperature for 5% mass loss observed by TGA at a heating rate of 10K min⁻¹. ^c Values obtained after Soxhlet extraction in THF for 24 h on a set of four samples. ^d Obtained from uniaxial tensile measurements at room temperature with a rate of 10 mm/min on a sample set of at least 5. ^e Not determined.

After confirming good network formation, Soxhlet extraction experiments in THF (at 66 °C) for 24 h were conducted to verify strong network integrity. With soluble fractions well below 10 %, these first qualitative measurements indicate that the formation of sulfonyl isocyanate intermediates are short-lived and did not result in complete dissolution of the polymer network. Moreover, analysis of the soluble fraction of PUSU-20 by ¹H-NMR did not reveal any signals originating from the blocked reactive adduct (**Figure S26**).

A distinct trend in the mechanical properties could also be observed when increasing the amount of SU units in the modified PU materials, as measured *via* uniaxial tensile tests (**Figure 4** and **Figure S27**). For example, the Young's modulus almost doubled from PUSU-5 to PUSU-20 (2.1 MPa to 4.1 MPa). Moreover, a gradual increase in strain and stress at break could be detected up to 237 % and 4.8 MPa, respectively. The increase in tensile properties is clearly related to the self-complementary hydrogen bonding of the SUs.⁶⁴ The improved mechanical performance can therefore be explained by the inclusion of the more acidic SU domains, which enable strong hydrogen bonding in an otherwise flexible, apolar matrix.

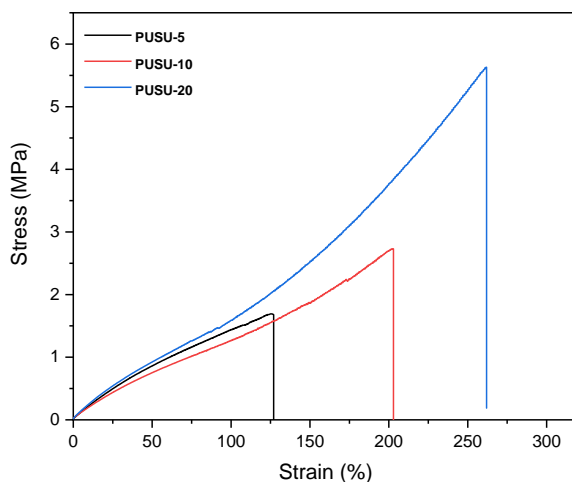


Figure 4. Stress strain curves obtained from uniaxial tensile measurements of the PUSU materials, showing a significant improvement when increasing SU content.

To determine changes in viscoelastic behavior when including reversible SU units, stress-relaxation experiments were performed from 150 to 100 °C (**Figure 5**). Importantly, as discussed in seminal work of Flory on the rubber elasticity theory,⁷⁰ it was necessary to evaluate non-normalized relaxation values to reveal any cross-linking density changes due to (sulfonyl) isocyanate deblocking during the measurement. Similar trends are observed in frequency sweep measurements (**Figure S28**). As such, variations in both the modulus ($G[T]$, y-axis) and relaxation time ($\tau[T]$, x-axis) could be determined as a function of temperature and SU content. Distinct viscosity values ($\eta[T]$) could then be calculated from the Maxwell relation $\eta[T] = G\tau$, which allowed to make a better comparison than considering the impact on relaxation time $\tau[T]$ alone.^{54,71}

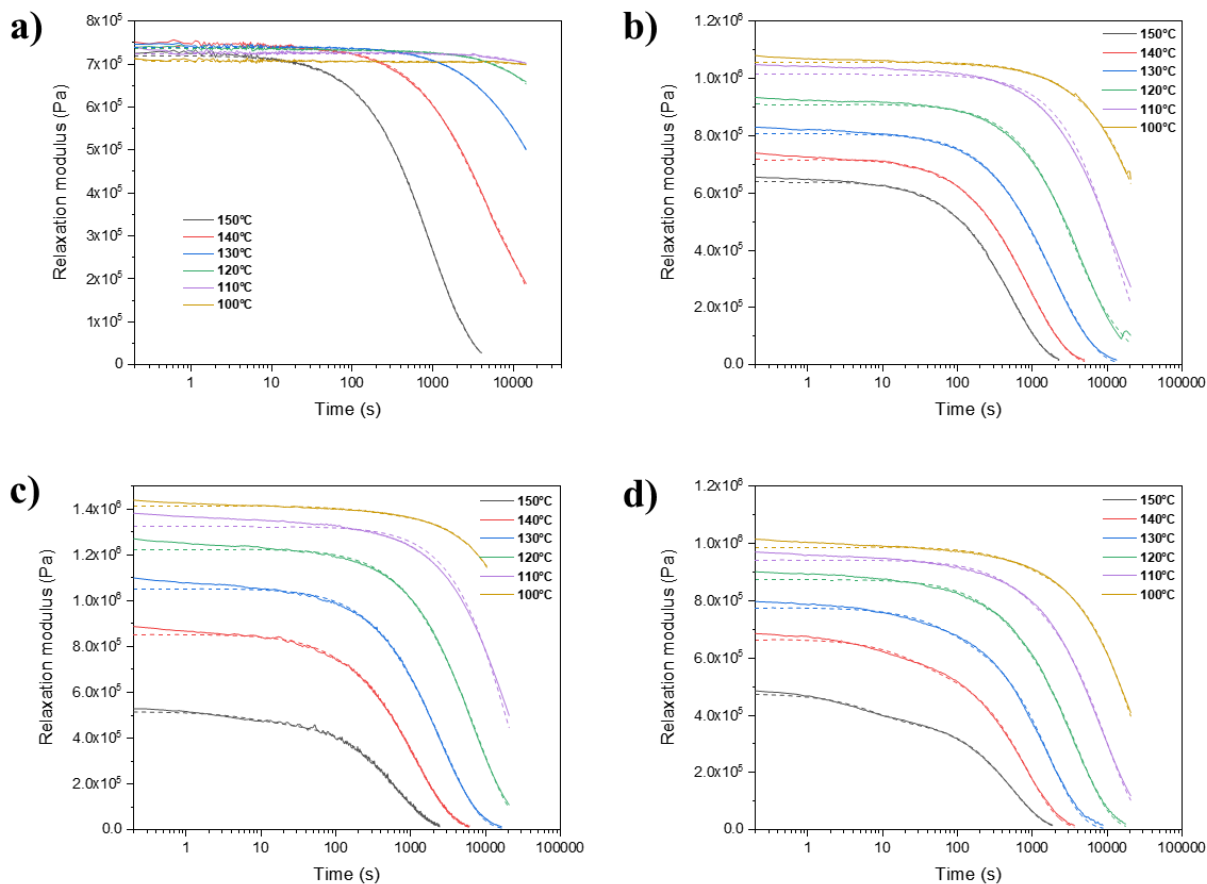


Figure 5. Non-normalized stress relaxation plots of PUSU-0 (a), PUSU-5 (b), PUSU-10 (c) and PUSU-20 (d) from 150 to 100°C; the fitting with a Maxwell model containing two elements is given in dashed lines.

When analyzing the relaxation curves of PUSU-0 (**Figure 5a**), the first obvious observation are the long relaxation times ($> 10\,000$ s, **Table S6**) and only a minor variation in cross-linking density. In light of the negative compression molding and relaxation results, we reasoned that any “processability” of (elastomeric) conventional PU materials could be mostly explained by unavoidable network defects. These results demonstrate why direct (catalyzed) urethane exchange

still needs additional mechanistic research efforts to become a more viable PU recycling strategy.^{39,40}

Notably, introducing SU bonds had a significant impact on both the modulus and relaxation time of the modified PU networks (**Figure 5b-d**). Furthermore, structural differences in the material exist as the deblocked sulfonyl isocyanate is much more reactive compared to the regular deblocked isocyanates (*i.e.* a chemically heterogeneous network), resulting in two relaxation modes with distinct chemical reactivity differences. Moreover, this effect became even more pronounced when increasing the relative SU content. Our research group recently published on a rheological study, where we demonstrate how these relaxation modes (*i.e.* macroscopic response) can be analyzed and linked to a specific reactive segment (*i.e.* microscopic structure) to measure reactivity changes in polymer networks.⁷¹ Specifically, while the single-element Maxwell model is often a good starting point (**Eq S4, Figure S29**), using a two-element Maxwell model (**Eq 1**) is much more accurate in many cases. Here, one element can be linked to the more reactive segments, while another element can be linked to the less reactive segments.

$$G(t) = G_{0,fast} e^{\frac{-t}{\tau_{fast}}} + G_{0,slow} e^{\frac{-t}{\tau_{slow}}} \quad (\text{Eq 1})$$

We rationalized that the more reactive element should correspond to the SU bonds based on two important factors. Firstly, sulfonyl isocyanates are roughly 100 times more reactive than regular isocyanates.^{22,56} Secondly, the weight of the fast relaxing element to the total relaxation curve corresponds well to the relatively low fraction of SU units in the material.

In isocyanate-based dynamic covalent networks, it can be expected that multiple reaction pathways for the reformation of network bonds are always competing, making interpretation of molecular

parameters (*e.g.* enthalpy or entropy values) of a specific relaxation mode difficult. However, based on the experimental data, some more general observations can be made and the dominant pathways rationalized. Viscosity values ($\eta[T]$) can be calculated based on the stress relaxation by simply multiplying G_0 with $(\tau_{slow} + \tau_{fast})$ (**Table S6**). Flow activation energies ($E_{a,flow}$) can be calculated from the viscosity by plotting $\ln(\eta)$ against $1000/T$ in an Arrhenius plot (**Figure 6b** and **Table 2**). As a result of faster relaxation and more pronounced decrosslinking, $E_{a,flow}$ almost halved already after the introduction of only 5% SU. Moreover, a further decrease is visible when more SU is incorporated, indicating that even a small amount of SU bonds has a positive effect on the overall (re)processability of the PU samples, and thus making clear that the dynamicity in the presented PUSU materials is governed by a specific degree of PU and SU kinetics.

Table 2. Summary of the rheological results of the N-sulfonyl urethane containing materials.

Network	$E_{a,slow}$ (kJ mol ⁻¹) ^(a)	$E_{a,fast}$ (kJ mol ⁻¹) ^(a)	$E_{a,flow}$ (kJ mol ⁻¹) ^(b)	G' (kPa) ^(c)	G' (kPa) ^(d)
PUSU-0	252.36±54.52 ^(e)	143.26±45.15	238.90±52.23	314	429
PUSU-5	139.58±8.42	112.45±14.54	155.42±14.12	463	1155
PUSU-10	117.59±4.39	226.84±52.32	164.65±4.30	577	937
PUSU-20	99.45±5.41	163.01±13.97	124.33±2.39	542	902

^a Activation energies obtained from Arrhenius plots after stress relaxation measurements and fitting with a generalized Maxwell model with two elements. ^b Flow activation energies obtained from viscosity values ^c Plateau storage modulus obtained from frequency sweep measurements at 150°C and 1 rad.s⁻¹. ^d Plateau storage modulus obtained from frequency sweep measurements at 100°C and 1 rad.s⁻¹. ^e Calculated using extrapolated values.

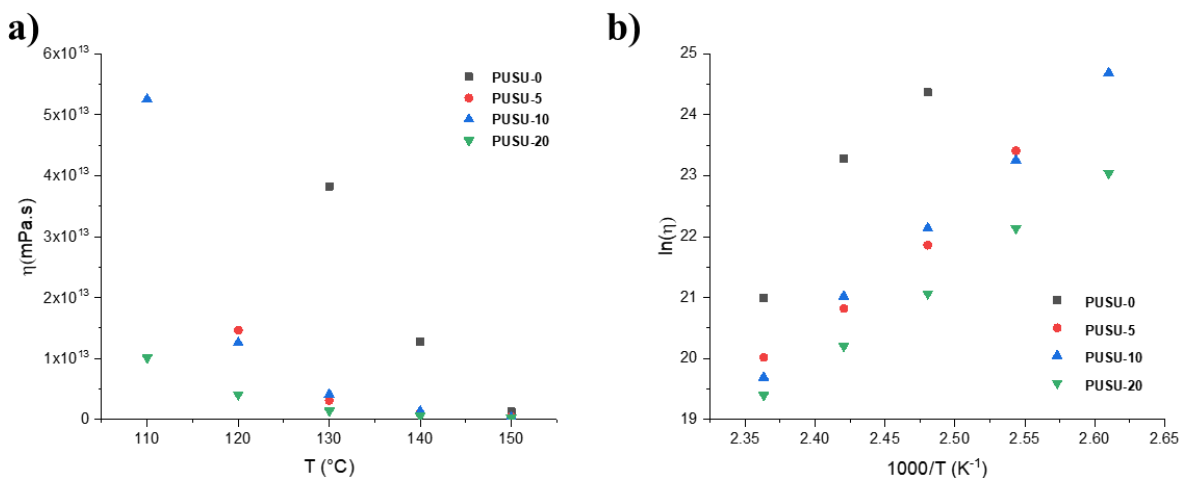
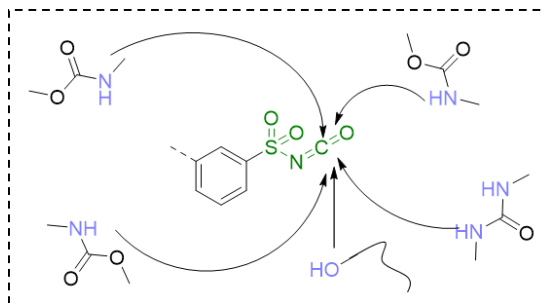


Figure 6. a) Viscosity values as a function of temperature for the sulfonyl urethane containing materials and related Arrhenius plots (b).

Critically, it can be expected that the reversal of sulfonyl urethane bonds, which deblocks the reactive sulfonyl isocyanates, can lead to side reactions, just as is known normal isocyanates. The lower temperature could help to limit these side reactions, but our data indicates that the dynamic covalent behavior indeed involves more than simple deblocking and recombining to hydroxyls, as some properties do change over multiple cycles (**Scheme 2**). If the sulfonyl isocyanate reacts partially with the surrounding urethane or urea bonds, allophanate or biuret structures could form, leaving a dangling alcohol chain behind (**Scheme 2**). Nonetheless, we expect that the reversibility of these “secondary products or cross-links” is also highly facilitated by the electron-withdrawing sulfonyl group, which can then promote reversion or alcohol exchange alone. In this way, this new chemistry to improve PU (re-)processability has an important advantage over approaches wherein the reversibility of the urethane bond is promoted by reacting it with a hindered or more readily eliminated nucleophile (hindered amine, thiols, ...).



Scheme 2. Possible side reactions of the deblocked sulfonyl isocyanate with surrounding urethanes and ureas in the polyurethane materials, leaving a dangling alcohol group behind.

The potential side reactions could influence both storage and loss modulus of the materials, which is often undesirable. In an effort to investigate the side reactions that produce these secondary products, a time sweep experiment was conducted at 140°C on both PUSU-0 and PUSU-10. For both materials, a slight increase in G' is observed, indicating that an increase in cross-link density is occurring (**Figure S30**). Repeated stress-relaxation experiments at 150°C, a temperature where fast relaxation occurred for both materials, were used to probe this aging behavior. While relaxation is still occurring, an increase in modulus over the cycles is visible for both materials (**Figure S31**).

As mentioned above, hydrolysis is a valid concern in the PUSU materials. Therefore, as proof-of-principle, a sample of PUSU-20 was submerged in water at 100°C for 16 hours after which a stress-relaxation experiment on the dried sample was conducted. The relaxation behavior before and after showed to be very similar (**Figure S32** and **Table S7**).

Finally, in order to demonstrate the improved recyclability of PUs containing sulfonyl urethanes, the materials were subjected to multiple cutting and remolding steps. On the one hand, the properties of the PUSU-20 materials decreased over the reprocessing cycles (**Table S8** and **Figure**

S33-38). This could most likely be attributed to the above mentioned side reactions of the deblocked sulfonyl isocyanates. Moreover, after $^1\text{H-NMR}$ analysis of the soluble fraction of the recycled PUSU-20, signals from a degradation product of **7** are visible (**Figure S37**). On the other hand, PUSU-5 and PUSU-10 showed to be recyclable at least three times, as evidenced by only a small change in thermal, mechanical and rheological properties (see Supporting Information, **Table S9, Figure S39-44, Table S10, Figure 45-50 and Table S11**). Under the same conditions, PUSU-0 was not processable, which demonstrates that the introduction of SU-moieties indeed improved the overall (re-)processability of PU matrices.

CONCLUSION

In summary, blocked sulfonyl isocyanates were investigated as dynamic motifs in covalent adaptable polyurethane networks. Exchange reactions of blocked sulfonyl isocyanates (*i.e.* sulfonyl urethanes) were observed on small molecule level, with an activation energy of 77 kJ mol^{-1} , while no exchange was observed for regular urethanes. Elastomeric, hydrophobic regular PU-based CANs with small amounts of these sulfonyl urethane moieties embedded as dynamic chain extenders (5, 10 and 20%) were prepared in a straightforward fashion and compared to reference polyurethanes with similar composition. Increasing the sulfonyl urethane content in the materials positively influenced the tensile properties because of the increased hydrogen bonding. Rheological experiments were used to investigate the viscoelastic characteristic of the materials and revealed a complex behavior, that could be described by a Maxwell model containing two elements, indicating the influence of the two dynamic chemistries ('native urethanes' and sulfonyl urethanes). Finally, we could confirm that incorporation of only small amounts of these sulfonyl urethane bonds in polymer networks is beneficial for their recycling under milder conditions and

further investigations into this attractive dynamic chemistry platform is currently underway and will be reported in due course.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information, containing details about instrumentation, synthesis procedures, ^1H - and ^{13}C -NMR spectra, IR spectra, DSC, DMTA and TGA thermograms, stress relaxation data, frequency sweep and time sweep measurements of (re)processed materials is available free of charge.

AUTHOR INFORMATION

Corresponding Author

* Filip E. Du Prez - Polymer Chemistry Research group, Centre of Macromolecular Chemistry (CMaC), Department of Organic and Macromolecular Chemistry, Faculty of Sciences, Ghent University, Krijgslaan 281-S4, Ghent, 9000, Belgium; orcid.org/0000-0001-7727-4155;

Email: filip.duprez@ugent.be

* Johan M. Winne - Laboratory of Organic Synthesis, Department of Organic and Macromolecular Chemistry, Faculty of Sciences, Ghent University, Krijgslaan 281-S4, Ghent, 9000, Belgium; orcid.org/0000-0002-9015-4497

Email: Johan.winne@ugent.be

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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REFERENCES

- (1) Sonnenschein, M. F. *Polyurethanes: Science, Technology, Markets and Trends*; John Wiley & Sons, Inc: Hoboken NL, 2014.
- (2) Adam, N.; Avar, G.; Blankenheim, H.; Friederichs, W.; Giersig, M.; Weigand, E.; Halfmann, M.; Wittbecker, F.-W.; Larimer, D.-R.; Maier, U.; Meyer-Ahrens, S.; Noble, K.-L.; Wussow, H.-G. Polyurethanes. *Ullmann's Encycl. Ind. Chem.*; 2005.
- (3) Van Lijsebetten, F.; Debsharma, T.; Winne, J. M.; Du Prez, F. E. A Highly Dynamic Covalent Polymer Network without Creep: Mission Impossible? *Angew. Chemie Int. Ed.*

- 2022, 61 (48).
- (4) 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.
 - (5) Jourdain, A.; Asbai, R.; Anaya, O.; Chehimi, M. M.; Drockenmuller, E.; Montarnal, D. Rheological Properties of Covalent Adaptable Networks with 1,2,3-Triazolium Cross-Links: The Missing Link between Vitrimers and Dissociative Networks. *Macromolecules* **2020**, 53 (6), 1884–1900.
 - (6) Kloxin, C. J.; Bowman, C. N. Covalent Adaptable Networks: Smart, Reconfigurable and Responsive Network Systems. *Chem. Soc. Rev.* **2013**, 42 (17), 7161–7173.
 - (7) Scheutz, G. M.; Lessard, J. J.; Sims, M. B.; Sumerlin, B. S. Adaptable Crosslinks in Polymeric Materials: Resolving the Intersection of Thermoplastics and Thermosets. *J. Am. Chem. Soc.* **2019**, 141 (41), 16181–16196.
 - (8) Sridhar, L. M.; Oster, M. O.; Herr, D. E.; Gregg, J. B. D.; Wilson, J. A.; Slark, A. T. Re-Usable Thermally Reversible Crosslinked Adhesives from Robust Polyester and Poly(Ester Urethane) Diels-Alder Networks. *Green Chem.* **2020**, 22 (24), 8669–8679.
 - (9) Du, P.; Wu, M.; Liu, X.; Zheng, Z.; Wang, X.; Joncheray, T.; Zhang, Y. Diels-Alder-Based Crosslinked Self-Healing Polyurethane/Urea from Polymeric Methylene Diphenyl Diisocyanate. *J. Appl. Polym. Sci.* **2014**, 131 (9), 1–7.
 - (10) Zhang, G.; Zhao, Q.; Yang, L.; Zou, W.; Xi, X.; Xie, T. Exploring Dynamic Equilibrium of

- Diels-Alder Reaction for Solid State Plasticity in Remoldable Shape Memory Polymer Network. *ACS Macro Lett.* **2016**, *5* (7), 805–808.
- (11) Zhao, S.; Abu-Omar, M. M. Recyclable and Malleable Epoxy Thermoset Bearing Aromatic Imine Bonds. *Macromolecules* **2018**, *51* (23), 9816–9824.
- (12) Memon, H.; Liu, H.; Rashid, M. A.; Chen, L.; Jiang, Q.; Zhang, L.; Wei, Y.; Liu, W.; Qiu, Y. Vanillin-Based Epoxy Vitrimer with High Performance and Closed-Loop Recyclability. *Macromolecules* **2020**, *53* (2), 621–630.
- (13) Montarnal, D.; Capelot, M.; Tournilhac, F.; Leibler, L. Silica-Like Malleable Materials from Permanent Organic Networks. *Science (80-.)*. **2011**, *334* (6058), 965–968.
- (14) Self, J. L.; Dolinski, N. D.; Zayas, M. S.; Read De Alaniz, J.; Bates, C. M. Brønsted-Acid-Catalyzed Exchange in Polyester Dynamic Covalent Networks. *ACS Macro Lett.* **2018**, *7* (7), 817–821.
- (15) Chappuis, S.; Edera, P.; Cloitre, M.; Tournilhac, F. Enriching an Exchangeable Network with One of Its Components: The Key to High- TgEpoxy Vitrimers with Accelerated Relaxation. *Macromolecules* **2022**, *55* (16), 6982–6991.
- (16) Ruiz de Luzuriaga, A.; Martin, R.; Markaide, N.; Rekondo, A.; Cabañero, G.; Rodríguez, J.; Odriozola, I. Epoxy Resin with Exchangeable Disulfide Crosslinks to Obtain Reprocessable, Repairable and Recyclable Fiber-Reinforced Thermoset Composites. *Mater. Horizons* **2016**, *3* (3), 241–247.
- (17) Maes, S.; Scholiers, V.; Du Prez, F. E. Photo-Crosslinking and Reductive Decrosslinking

- of Polymethacrylate-Based Copolymers Containing 1,2-Dithiolane Rings. *Macromol. Chem. Phys.* **2022**, 2100445.
- (18) Ogden, W. A.; Guan, Z. Recyclable, Strong, and Highly Malleable Thermosets Based on Boroxine Networks. *J. Am. Chem. Soc.* **2018**, *140* (20), 6217–6220.
- (19) Saed, M. O.; Gablier, A.; Terentejv, E. M. Liquid Crystalline Vitrimers with Full or Partial Boronic-Ester Bond Exchange. *Adv. Funct. Mater.* **2020**, *30* (3), 1–8.
- (20) Brunet, J.; Collas, F.; Humbert, M.; Perrin, L.; Brunel, F.; Lacôte, E.; Montarnal, D.; Raynaud, J. High Glass-Transition Temperature Polymer Networks Harnessing the Dynamic Ring Opening of Pinacol Boronates. *Angew. Chemie - Int. Ed.* **2019**, *58* (35), 12216–12222.
- (21) Aguirresarobe, R. H.; Nevejans, S.; Reck, B.; Irusta, L.; Sardon, H.; Asua, J. M.; Ballard, N. Healable and Self-Healing Polyurethanes Using Dynamic Chemistry. *Prog. Polym. Sci.* **2021**, *114*, 101362.
- (22) Delebecq, E.; Pascault, J.; Boutevin, B.; Ganachaud, F. On the Versatility of Urethane/Urea Bonds: Reversibility, Blocked Isocyanate, and Non-Isocyanate Polyurethane. *Chem. Rev.* **2013**, *113* (1), 80–118.
- (23) Yoon, P. J.; Han, C. D. Effect of Thermal History on the Rheological Behavior of Thermoplastic Polyurethanes. *Macromolecules* **2000**, *33* (6), 2171–2183.
- (24) Colodny, P. C.; Tobolsky, A. V. Chemorheological Study of Polyurethan Elastomers 1. *J. Am. Chem. Soc.* **1957**, *79* (16), 4320–4323.

- (25) Offenbach, J. A.; Tobolsky, A. V. Chemical Relaxation of Stress in Polyurethane Elastomers. *J. Colloid Sci.* **1956**, *11* (1), 39–47.
- (26) 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.
- (27) Fortman, D. J.; Brutman, J. P.; Hillmyer, M. A.; Dichtel, W. R. Structural Effects on the Reprocessability and Stress Relaxation of Crosslinked Polyhydroxyurethanes. *J. Appl. Polym. Sci.* **2017**, *134* (45), 44984.
- (28) 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.
- (29) Wicks, D. A.; Wicks, Z. W. Blocked Isocyanates III: Part A. Mechanisms and Chemistry. *Prog. Org. Coatings* **1999**, *36* (3), 148–172.
- (30) Wicks, D. A.; Wicks, Z. W. Blocked Isocyanates III - Part B: Uses and Applications of Blocked Isocyanates. *Prog. Org. Coatings* **2001**, *41* (1–3), 1–83.
- (31) Liu, W. X.; Zhang, C.; Zhang, H.; Zhao, N.; Yu, Z. X.; Xu, J. Oxime-Based and Catalyst-Free Dynamic Covalent Polyurethanes. *J. Am. Chem. Soc.* **2017**, *139* (25), 8678–8684.
- (32) Quérat, E.; Tighzert, L.; Pascault, J.-P. Hydroxamic Acid Esters and Oximes as Isocyanate Blocking Agents. *Die Angew. Makromol. Chemie* **1994**, *219* (3835), 185–203.
- (33) Camberlin, Y.; Michaud, P.; Pesando, C.; Pascault, J. P. Isocyanate Blocking Agents Use

- in Polyurethane Processing. *Makromol. Chemie. Macromol. Symp.* **1989**, 25 (1), 91–99.
- (34) Fu, D.; Pu, W.; Escorihuela, J.; Wang, X.; Wang, Z.; Chen, S.; Sun, S.; Wang, S.; Zuilhof, H.; Xia, H. Acylsemicarbazide Moieties with Dynamic Reversibility and Multiple Hydrogen Bonding for Transparent, High Modulus, and Malleable Polymers. *Macromolecules*.
- (35) Mühlebach, A. Pyrazoles—A Novel Class of Blocking Agents for Isocyanates. *J. Polym. Sci. Part A Polym. Chem.* **1994**, 32 (4), 753–765.
- (36) Huang, S.; Podgórski, M.; Han, X.; Bowman, C. N. Chemical Recycling of Poly(Thiourethane) Thermosets Enabled by Dynamic Thiourethane Bonds. *Polym. Chem.* **2020**, 11 (43), 6879–6883.
- (37) Li, L.; Chen, X.; Torkelson, J. M. Reprocessable Polymer Networks via Thiourethane Dynamic Chemistry: Recovery of Cross-Link Density after Recycling and Proof-of-Principle Solvolysis Leading to Monomer Recovery. *Macromolecules* **2019**, 52 (21), 8207–8216.
- (38) Cui, C.; Chen, X.; Ma, L.; Zhong, Q.; Li, Z.; Mariappan, A.; Zhang, Q.; Cheng, Y.; He, G.; Chen, X.; Dong, Z.; An, L.; Zhang, Y. Polythiourethane Covalent Adaptable Networks for Strong and Reworkable Adhesives and Fully Recyclable Carbon Fiber-Reinforced Composites. *ACS Appl. Mater. Interfaces* **2020**, 12 (42), 47975–47983.
- (39) Fortman, D. J.; Sheppard, D. T.; Dichtel, W. R. Reprocessing Cross-Linked Polyurethanes by Catalyzing Carbamate Exchange. *Macromolecules* **2019**, 52 (16), 6330–6335.

- (40) Brutman, J. P.; Fortman, D. J.; De Hoe, G. X.; Dichtel, W. R.; Hillmyer, M. A. Mechanistic Study of Stress Relaxation in Urethane-Containing Polymer Networks. *J. Phys. Chem. B* **2019**, *123* (6), 1432–1441.
- (41) Zheng, N.; Hou, J.; Xu, Y.; Fang, Z.; Zou, W.; Zhao, Q.; Xie, T. Catalyst-Free Thermoset Polyurethane with Permanent Shape Reconfigurability and Highly Tunable Triple-Shape Memory Performance. *ACS Macro Lett.* **2017**, *6* (4), 326–330.
- (42) Zheng, N.; Fang, Z.; Zou, W.; Zhao, Q.; Xie, T. Thermoset Shape-Memory Polyurethane with Intrinsic Plasticity Enabled by Transcarbamoylation. *Angew. Chemie - Int. Ed.* **2016**, *55* (38), 11421–11425.
- (43) Shi, J.; Zheng, T.; Zhang, Y.; Guo, B.; Xu, J. Reprocessable Cross-Linked Polyurethane with Dynamic and Tunable Phenol-Carbamate Network. *ACS Sustain. Chem. Eng.* **2020**, *8* (2), 1207–1218.
- (44) Han, F.; Xu, B.; Shah, S. A. A.; Zhang, J.; Cheng, J. Thermally Reversible Crosslinked Polyurethanes Based on Blocking and Deblocking Reaction. *Macromol. Mater. Eng.* **2020**, *305* (5), 1–9.
- (45) Sheppard, D. T.; Jin, K.; Hamachi, L. S.; Dean, W.; Fortman, D. J.; Fortman, D. J.; Ellison, C. J.; Dichtel, W. R. Reprocessing Postconsumer Polyurethane Foam Using Carbamate Exchange Catalysis and Twin-Screw Extrusion. *ACS Cent. Sci.* **2020**, *6* (6), 921–927.
- (46) Chen, X.; Hu, S.; Li, L.; Torkelson, J. M. Dynamic Covalent Polyurethane Networks with Excellent Property and Cross-Link Density Recovery after Recycling and Potential for Monomer Recovery. *ACS Appl. Polym. Mater.* **2020**, *2* (5), 2093–2101.

- (47) Elizalde, F.; Aguirresarobe, R. H.; Gonzalez, A.; Sardon, H. Dynamic Polyurethane Thermosets: Tuning Associative/Dissociative Behavior by Catalyst Selection. *Polym. Chem.* **2020**, *11* (33), 5386–5396.
- (48) El-Zaatari, B. M.; Ishibashi, J. S. A.; Kalow, J. A. Cross-Linker Control of Vitrimer Flow. *Polym. Chem.* **2020**, *11* (33), 5339–5345.
- (49) Kang, B.; Kalow, J. A. Internal and External Catalysis in Boronic Ester Networks. *ACS Macro Lett.* **2022**, *11* (3), 394–401.
- (50) Schoustra, S. K.; Dijksman, J. A.; Zuilhof, H.; Smulders, M. M. J. Molecular Control over Vitrimer-like Mechanics-Tuneable Dynamic Motifs Based on the Hammett Equation in Polyimine Materials. *Chem. Sci.* **2021**, *12* (1), 293–302.
- (51) Van Herck, N.; Maes, D.; Unal, K.; Guerre, M.; Winne, J. M.; Du Prez, F. E. Covalent Adaptable Networks with Tunable Exchange Rates Based on Reversible Thiol–Yne Cross-Linking. *Angew. Chemie - Int. Ed.* **2020**, *59* (9), 3609–3617.
- (52) Herbert, K. M.; Getty, P. T.; Dolinski, N. D.; Hertzog, J. E.; de Jong, D.; Lettow, J. H.; Romulus, J.; Onorato, J. W.; Foster, E. M.; Rowan, S. J. Dynamic Reaction-Induced Phase Separation in Tunable, Adaptive Covalent Networks. *Chem. Sci.* **2020**, *11* (19), 5028–5036.
- (53) Ying, H.; Zhang, Y.; Cheng, J. Dynamic Urea Bond for the Design of Reversible and Self-Healing Polymers. *Nat. Commun.* **2014**, *5* (1), 3218.
- (54) 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.

- (55) Huang, D.; Yan, G. Recent Advances in Reactions of Aryl Sulfonyl Isocyanates. *Org. Biomol. Chem.* **2017**, *15* (8), 1753–1761.
- (56) Ulrich, H. The Chemistry of Sulfonyl Isocyanates. *Chem. Rev.* **1965**, *65* (43), 369–376.
- (57) McFarland, J. W. Sulfonyl Isocyanates and Sulfonyl Isothiocyanates. *Sulfur reports* **1981**, *1* (4), 215–262.
- (58) Isaksson, R.; Kumpina, I.; Larhed, M.; Wannberg, J. Rapid and Straightforward Transesterification of Sulfonyl Carbamates. *Tetrahedron Lett.* **2016**, *57* (13), 1476–1478.
- (59) Kumpina, I.; Isaksson, R.; Sävmarker, J.; Wannberg, J.; Larhed, M. Microwave Promoted Transcarbamylation Reaction of Sulfonylcarbamates under Continuous-Flow Conditions. *Org. Process Res. Dev.* **2016**, *20* (2), 440–445.
- (60) Manabe, S.; Yamaguchi, M.; Ito, Y. Sulfonylcarbamate as a Versatile and Unique Hydroxy-Protecting Group: A Protecting Group Stable under Severe Conditions and Labile under Mild Conditions. *Chem. Commun.* **2013**, *49* (75), 8332–8334.
- (61) Taylor, L. D.; Macdonald, R. J.; Rubin, L. E. Acidity and Stability of Sulfonyl Carbamates and Ureas. *J. Polym. Sci. Part A-1 Polym. Chem.* **1971**, *9* (10), 3059–3061.
- (62) Taylor, L. D.; Pluhar, M.; RUBIN, L. E. Reaction of Sulfonyl Isocyanates with Polymeric Alcohols to Produce a Polymeric Acid. *J. Polym. Sci. B Polym. Lett.* **1967**, *5* (1), 77–78.
- (63) Rousseau, R. W.; Callihan, C. D.; Daly, W. H. Sulfonyl Carbamate Derivatives of Cellulose. *Macromolecules* **1969**, *2* (5), 502–507.
- (64) Peng, C. C.; Abetz, V. A Simple Pathway toward Quantitative Modification of

- Polybutadiene: A New Approach to Thermoreversible Cross-Linking Rubber Comprising Supramolecular Hydrogen-Bonding Networks. *Macromolecules* **2005**, *38* (13), 5575–5580.
- (65) Chen, Y.; Wu, W.; Wang, J.; Jiang, H.; Gao, Y. Synthesis and Properties of Thermoreversible Crosslinking Supramolecular Polymer with Weak Multiple-Hydrogen Bonds and Small Chemical Network Sites from Dimer Acid, Diamine and Sulfonyl Isocyanate. *J. Polym. Res.* **2011**, *18* (6), 2325–2333.
- (66) Houck, H. A.; De Bruycker, K.; Barner-Kowollik, C.; Winne, J. M.; Du Prez, F. E. Tunable Blocking Agents for Temperature-Controlled Triazolinedione-Based Cross-Linking Reactions. *Macromolecules* **2018**, *51* (8), 3156–3164.
- (67) 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).
- (68) Van Lijsebetten, F.; De Bruycker, K.; Winne, J. M.; Du Prez, F. E. Masked Primary Amines for a Controlled Plastic Flow of Vitrimers. *ACS Macro Lett.* **2022**, *11* (7), 919–924.
- (69) Houck, H. A.; De Bruycker, K.; Billiet, S.; Dhanis, B.; Goossens, H.; Catak, S.; Van Speybroeck, V.; Winne, J. M.; Du Prez, F. E. Design of a Thermally Controlled Sequence of Triazolinedione-Based Click and Transclick Reactions. *Chem. Sci.* **2017**, *8* (4), 3098–3108.
- (70) Flory, P. J. Network Structure and the Elastic Properties of Vulcanized Rubber. *Chem. Rev.* **1944**, *35* (1), 51–75.

- (71) Van Lijsebetten, F.; De Bruycker, K.; Van Ruymbeke, E.; Winne, J. M.; Du Prez, F. E. Characterising Different Molecular Landscapes in Dynamic Covalent Networks. *Chem. Sci.* **2022**, *13* (43), 12865–12875.