Bio-based, creep-resistant covalent adaptable networks based on β-amino ester chemistry

*Lucas Stricker‡, Christian Taplan‡ and Filip E. Du Prez**

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

* *E-Mail: filip.duprez@ugent.be*

KEYWORDS

Covalent adaptable networks, Recycling, Renewable resources, Creep resistant networks, *β*-amino esters

ABSTRACT

For this study, creep resistant covalent adaptable networks were prepared making use of the reversible *β*-amino ester chemical platform and starting from bio-based raw materials with an overall bio-based carbon content of >90%. The investigated materials were synthesized with different crosslinking densities in a solvent-free fashion. The applied building blocks consisted of an easily obtained acrylate, based on a bio-based diol, and a commercially available bio-based multifunctional amine. Following their synthesis, the materials were investigated with regard to their thermal, thermo-mechanical and rheological properties, which were preserved after up to three reprocessing cycles. Moreover, the obtained elastomers showed high thermal stability, in combination with good reprocessability at 180°C and excellent creep resistance at elevated temperatures up to 120°C.

INTRODUCTION

Nowadays life is unthinkable without the myriad of polymer materials that are used in our daily lives in countless applications such as packaging, transportation, electronic devices, or numerous other plastic-based materials.[1,2] Often, these polymer materials are playing a crucial role in these kinds of applications ensuring high efficiency, low costs or allowing lightweight construction only to name a few.[3–5] Nevertheless, the increasing plastic pollution and the depletion of fossil resources are huge economic and environmental issues, causing the need for efficient recycling methods and sourcing of raw materials from renewable resources.[6,7]

While thermoplastics are moldable and malleable when being heated and consequently offer in principle facile recycling options, no such straightforward option is available for thermosetting materials, which consist of a permanent three-dimensional covalent network. As a result of the network structure however, thermosets offer superior properties compared to thermoplastics enabling high chemical and mechanical durability and dimensional stability. Yet, it is exactly the high resistance and the permanent character of the network structure that makes recycling very challenging. Consequently, thermosets often go to waste or are being incinerated.[8] In the context of the new plastics economy vision, the scientific community as well as the industry is seeking for strategies to overcome the aforementioned issues of thermosetting materials.[9]

On the one hand, due to the finite fossil resources such as crude oil and gas, the demand for new, more sustainable and renewable raw materials as functional building blocks for polymer materials is significantly increasing.[10] Consequently in recent years thermoset materials have been prepared from vegetable oil,[11,12], eugenol[13,14] lignin,[15] vanillin,[16] and isosorbide.[17] With tailored molecular design, these materials exhibit physical properties that are comparable to their petrochemical-derived counterparts, showing promise in future applications. On the other hand, one strategy to enhance recyclability of thermosetting materials is the implementation of reversible covalent bonds in thermoset materials, making network rearrangements and potentially thermoplastic behavior upon application of a stimulus possible.[18–21] Although it was already reported decades ago that cross-linked rubbers using disulfide bonds and silyl ethers showed the dissipation of stress by thermally activated bond rearrangement,[22–25] only in recent years, more efforts were put on the development of so-called covalent adaptable networks (CANs), fueled by the increasing plastic pollution issue describe above.[9,26,27] Several dynamic chemical reactions have been reported including disulfides[28–30], silyl ether exchange,[31,32] trans(thio)esterification,[33–36], transamination[37–40], transalkylation,[41–43] reversible cycloadditions,[20,44] and others.[45–48] Many of those chemistry platforms have also been highlighted in recent reviews.[21,49–51]

Recently, *β*-amino esters were reported as a thermally dynamic motif for the design of CANs.[52–54] These *β*-amino esters are readily prepared by abundantly available building blocks using the aza-Michael reaction of an amine to an acrylate, making them a new promising motif to create dynamic polymer materials, with good thermal and hydrolytic stability.[52] Despite the fact that the aza-Michael reaction was widely explored and studied previously, it was usually considered to create permanent bonds in bulk materials.[55,56] However, recently published studies showed that *β*-amino esters undergo both dynamic aza-Michael reaction and – in the presence of free hydroxyl groups – a catalyst-free transesterification.[52–54]

As described above, the development of recyclable and reprocessable covalently crosslinked networks, as well as the construction of polymers from renewable resources, are both stimulated by the economic and environmental problems associated with traditional thermoset materials. Consequently, efforts to combine these two strategies in material design for sustainable thermosets were already carried out with a focus on epoxy matrices[57] and accessible transamination-based chemistry systems,[58,59] A comprehensive overview of the state-of-the-art in combining reprocessable and renewable research strategies in the area of CANs are described in a recent review by *Avérous and co-workers*.[60] While several bio-based CANs have been reported recently, it should be noted that these materials are often only partially bio-based or involve (multi-)step derivatization of bio-derived raw materials into functional building blocks, decreasing the overall sustainability. Additionally, many of the reported CANs are by far outcompeted by classical thermosets with regard to long-term stability (e.g., hydrolytic and thermal stability). Finally, they typically suffer from a limited creep resistance, which hampers their potential industrial application.

In this context, we describe in this study *β*-amino ester-based CANs with excellent thermal stability and, for low T_g materials, remarkable creep resistance while showing swift recyclability thanks to the applied retro-aza-Michael chemical platform. Moreover, the investigated materials are prepared starting from Pripol and Priamine, both fatty acid derived compounds, and commercial building blocks, yielding an overall bio-based carbon content of at least 90%. By variation of the ratio of amine to acrylate groups, CANs with different cross-linking densities were obtained. As illustrated in Figure 1, every primary amine group can react with two acrylate groups.

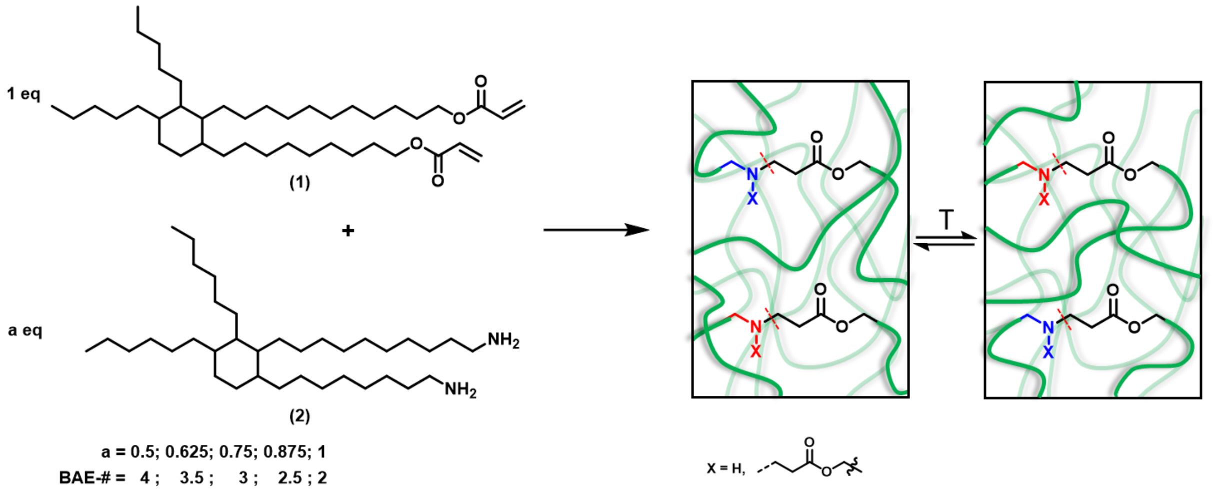


Figure 1. Representation of the *β*-amino ester network's formation from a biobased diacrylate (**1**) and Priamine (**2**), and of the rearrangement at elevated temperature.

It will be demonstrated that all materials are showing excellent thermal and rheological properties, thanks to the robust exchange reactions, further showcasing the potential of *β*-amino ester networks as sustainable CANs, which can be made from a broad set of commercially available (bio-based) amines and acrylates.

EXPERIMENTAL SECTION

Materials.

Acryloyl chloride 97.0%, (contains <210 ppm MEHQ as stabilizer) was purchased from Sigma-Aldrich. Tetrahydrofuran (THF), dichloromethane (DCM), anhydrous triethylamine 99.7%

(Et_3N), and acrylic acid 98% (contains 180 to 220 ppm MEHQ as stabilizer) were purchased from Acros Organics. Phenothiazine >98% and *p*-toluenesulfonic acid monohydrate >98% (*p*TsOH) were purchased from TCI. Pripol 2033 and Priamine 1074 were kindly provided by Croda. All reagents were used without further purification unless stated otherwise.

Instrumentation.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Advance Ultrashield 300 MHz spectrometer. Deuterated chloroform ($CDCl_3$) was used as the solvent in each sample. Chemical shifts are given in parts per million (ppm).

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) spectra were measured using a Perkin-Elmer Spectrum1000 FTIR infrared spectrometer with a diamond ATR probe.

Thermogravimetric analyses (TGA) were performed with a Mettler Toledo TGA/SDTA851e instrument under nitrogen atmosphere at a heating rate of 10 $K\cdot min^{-1}$ from 25 to 800°C.

Differential scanning calorimetry (DSC) analyses were performed with a Mettler Toledo instrument 1/700 under nitrogen atmosphere at a heating rate of 10 $K\cdot min^{-1}$ from -100 to 100°C.

Rheology experiments were performed on an Anton Paar MCR 302. The experiments were performed in parallel plate geometry using 8 mm sample disks. Unless otherwise specified, the experiments were performed using a normal force of 1 N, an oscillating frequency of 1 $rad\cdot s^{-1}$, and a strain of 1% was applied. For all rheology experiments, the applied stress comprised the linear viscoelastic region at the measured temperatures.

For **stress relaxation experiments**, a strain of 1% respectively was applied to the material and the relaxation modulus (G(t)) was followed over time at a constant temperature. The obtained characteristic relaxation time (τ*) was used to calculate an activation energy.

Creep experiments were performed by applying no strain for a duration of 300 s, which was followed by applying 2 kPa shear stress for 3600 s and a recovery period of 3800 s at 80 °C, 100 °C and 120 °C. Creep recovery measurements were preceded by a measurement at 80 °C to remove a possible thermal history.

Dynamic mechanical analysis (DMA) was performed on a DMA/SDTA861e from Mettler-Toledo utilizing two round samples (each *ca.* 1.75 mm (T) and 8.0 mm (D)) for application in the shear clamp. A temperature ramp was performed from -100 °C to +100 °C at a rate of 3 $\mathrm{K\cdot min^{-1}}$ with a displacement amplitude of 2 µm, a force amplitude of 5 N and a regular frequency of 1 Hz.

Reprocessability. To reprocess the network, the CAN was broken into pieces and placed into a rectangular mold (A, 70 mm × 40 mm × 2 mm; B, 30 mm × 15 mm × 2 mm) for compression molding. This assembly was placed in a 180 °C (Materials BAE-4, BAE-3.5, BAE-3, BAE-2.5) or 150°C (Material BAE-2) preheated compression press for 1 min under 0.5 metric tons of pressure. Then the pressure was increased to 4 tons and kept constant for an additional 59 min. After 60 min of pressing in total, the sample was carefully removed from the mold while still heated and in its elastic state.

Swelling tests were performed by immersing a sample of 40−60 mg in 3 mL of THF at room temperature for 5 days, and the swelling ratio was calculated using equation (1). Afterwards the samples were dried under vacuum for 2 days at 70°C. The soluble fraction was calculated using equation (2).

$$swelling\ ratio\ (\%) = 100 \times \frac{(m_s - m_i)}{m_i} \qquad (1)$$

$$soluble\ fraction\ (\%) = 100 \times \frac{(m_i - m_d)}{m_i} \qquad (2)$$

with m_i, m_s, and m_d being the initial, swollen, and dry mass, respectively.

Synthesis Methods:

Synthesis of Pripol 2033 acrylate (1). Method A: Pripol 2033 (20 g, 37.25 mmol, 1 eq.) was dissolved in DCM (100 mL) and cooled to 0°C in an ice-bath. To this solution Et_3N (15 mL, 108 mmol, 2.9 eq.) and acryloyl chloride (6.69 mL, 82 mmol, 2.2 eq.) were added sequentially. The solution was stirred for 1 h at 0°C and then allowed to warm to room temperature overnight. Water (50 mL) was added to quench remaining acryloyl chloride and the layers were separated. The organic layer was washed with aq. HCl (1M, 2 x 100 mL), aq. $NaHCO_3$ (3 x 100 mL) and brine (100 mL) and dried over $MgSO_4$. Removal of the solvent in vacuo yielded the desired Pripol acrylate (**1**) as yellowish liquid (24 g, quantitative yield).

Method B: A round-bottom flask was charged with a mixture of Pripol 2033 (4 g, 7.45 mmol, 1 eq.), acrylic acid (3.1 mL, 44.7 mmol, 6 eq.), $MgSO_4$ (100 wt%), *p*TsOH (26 mg, 0.15 mmol, 0.02 eq.) as catalyst and phenothiazine (0.05 g) to inhibit spontaneous polymerization. The mixture was heated to 100 °C for 24 h. After cooling to room temperature, DCM (50 mL) was added, the resulting suspension was filtered, and the filtrate was washed with $NaHCO_3$ (2 x 50 mL) to remove the excess of acrylic acid. After drying over $MgSO_4$ and drying *in vacuo* the desired Pripol acrylate (**1**) was obtained as orangish liquid (3.12 g, 4.84 mmol, 65 % yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.40 (dd, *J* = 17.3, 1.6 Hz, 2H), 6.12 (dd, *J* = 17.3, 10.4 Hz, 2H), 5.81 (dd, *J* = 10.4, 1.6 Hz, 2H), 4.15 (t, *J* = 6.7 Hz, 4H), 1.66 (p, *J* = 7.1 Hz, 4H), 1.27 (m, 40H), 0.87 (m, 6H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) *δ* = 166.50, 130.54, 128.83, 64.88, 32.08, 29.86, 29.68, 29.42, 28.78, 26.09, 22.85, 14.27 ppm.

Synthesis of *β*-amino ester materials. For the preparation of the materials in this study the bis-functional Pripol acrylate **1** (typically 4 g, 1 eq.) and bis-functional Priamine 1074 **2** (1 eq. (BAE-2), 0.875 eq. (BAE-2.5), 0.75 eq. (BAE-3), 0.625 eq. (BAE-3.5) or 0.5 eq. (BAE-4)) were mixed in a polypropylene cup using a DAC 150.1 FVZ speed mixer (typical conditions of mixing: 2 min with a speed of 2500 rpm). The obtained homogenous solution was cured at 70°C for 48 h to complete network formation. Hereafter, the polypropylene vial was broken, the sample was removed, broken into pieces, and pressed separately in steel molds, following the aforementioned reprocessing procedure.

RESULTS AND DISCUSSION

Monomer and material synthesis. As initial step in this study, the bio-based acrylate monomer (**1,** Figure 1) was synthesized in a straightforward and scalable one-step procedure from Pripol 2033. For that, a well-established procedure was used by simply reacting Pripol 2033 with a slight excess of triethylamine and acryloyl chloride in dichloromethane. Followed by an aqueous work-up, the desired acrylate (**1**) could then be isolated in quantitative yield and with extremely high purity in a scalable fashion (see Figure S1 and S2 for NMR spectra). While this method gives excellent results in terms of yields, purity, and possible scalability, it uses chlorinated solvents and toxic reagents. This, combined with the formation of hydrochloric acid as side product, reduces the sustainable aspect of this synthetic procedure.

As a consequence, we investigated the possibility of synthesizing Pripol acrylate (**1**) using a much more sustainable synthesis procedure that was recently reported for terpenoid-based acrylates by our group.[61] In this method, the synthesis starts from the alcohol precursor and acrylic acid, and only requires the use of a drying agent and a catalyst without the need for additional solvents. Additionally, water was found to be the only side product, therefore, this method was considered as being the most sustainable for the synthesis of several acrylates according to the CHEM21 green metrics toolkit. While in the previous study monofunctional acrylates were synthesized in good yields after a vacuum distillation work-up (60-80%), some adaptations had to be done for the synthesis of the Pripol acrylate (**1**). Indeed, the resulting bis-acrylate could not be isolated by a simple vacuum distillation due to its high boiling point. Therefore, the reaction had to be pushed to full conversion with a larger excess of acrylic acid (3 eq. per OH) in order to allow the isolation of the acrylate by a simple aqueous work-up. In this manner, the desired acrylate could be isolated in good yields (65%). While this procedure yielded the desired acrylate (**1**), the ^{1}H-NMR analysis also showed some additional signals at ~4.45 and ~2.70 ppm (Figure S3) from unwanted side products, hence resulting in a significantly lower purity compared to the method using acryloyl chloride. This result shows that a more sustainable synthesis of the Pripol-based acrylate (**1**) is possible, but it would need further optimization to avoid side products. Thus, in what follows, only the Pripol acrylate (**1**) obtained from the method involving acryloyl chloride was used for material preparation to exclude the potential influence of side products on the material properties of the β-amino ester networks.

After the successful synthesis of the Pripol acrylate (**1**), the *β*-amino ester-based networks could be prepared in analogous fashion to our previously published procedure by simply mixing the acrylate monomer (**1**) and the readily available bio-based bis-amine Priamine 1074 (**2**) in different ratios and curing at 70°C for 48 hours *via* the aza-Michael reaction, yielding elastic materials that could be easily reprocessed in transparent plates (Figure 1). The ratio of bis-acrylate (**1**) and bis-amine (**2**) has been chosen from 1:0.5 - representing a densely crosslinked network, since every amine can in principle react with two acrylate moieties – up to 1:1, which would create a linear polymer in the ideal case (Figure 1 left side). All of the obtained materials investigated in this study are composed of 90 to 92% bio-based carbon content, with the remaining 8 to 10% fossil-based carbon originating from the acrylate functionality. Although considerable effort has been put into the development of environmentally friendly and safer synthesis methods of acrylates, there is so far a lack of bio-based acrylating agents.[62] It should be noted that much research is ongoing to derive also acrylic acid industrially from bio-based raw materials such as lactic acid, which could further maximize the bio-content of such CANs.[63] During this study, the resulting materials are named according to the average expected reactions of the diamine (**2**) to the diacrylate (**1**). In composition BAE-2, an equimolar ratio of Priamine 1074 (**2**) (expectedly reacting twice) and Pripol-based diacrylate (**1**) is used, while BAE-4 contains an equimolar amount of amino-protons (expected functionality of Priamine 1074 is four in this case) to acrylates in the reaction mixture.

Material characterization. Initially, network formation and thermal properties of the synthesized BAE materials were investigated. An overview of the corresponding results is listed in Table 1 and Figure 2. Completion of curing was confirmed by ATR-FTIR spectroscopy, showing the vanishing of the C=C band of the acrylate at 1650 cm^{-1} and the typical shift of 10 cm^{-1} of the C=O band from 1725 cm^{-1} to 1734 cm^{-1} confirming the consumption of the acrylate groups when forming the corresponding *β*-amino ester network (Figure 2a). Network formation was additionally verified by swelling experiments in THF, yielding low soluble fractions for BAE-4, BAE-3.5 and BAE-3 of around 2%. For network BAE-2.5, a slightly higher soluble fraction (~5%) was obtained due to the lower crosslinking density. Although in theory the equimolar composition of diacrylate (**1**) and diamine (**2**) in BAE-2 should only result in a linear and fully soluble polymer and thus not yield a three-dimensional network, only a soluble fraction of 22% has been measured (see Table 1). This could be explained by a partial double aza-Michael addition on the same amine, yielding a crosslinking point, or by the presence of a small number of side-reactions such as amidation. In these cases, hyperbranched or loosely crosslinked networks/materials are obtained. As expected, a similar trend was observed in the swelling degree of the materials, yielding values of ~200% for BAE-4, BAE-3.5 and BAE-3, while BAE-2.5 (~320%) and BAE-2 (~800%) show significantly higher swelling ratios with decreasing crosslinking density (Table 1). In identical fashion, hydrolysis tests were performed by immersing ~20 mg of BAE-3 in 3 mL of demineralized water for 24 h at room temperature, as well as 100°C, followed by drying the samples in a vacuum oven at 120 °C and determining the respective soluble fraction and swelling ratio. As a result of their hydrophobic matrix, the materials remained visibly intact even in boiling water, showing moderately low swelling ratios of ~23% in either case and remarkably low soluble fractions (< 0,3%), showcasing that hydrolytic stability for such activated esters may be preserved when embedded in a hydrophobic polymer matrix.

The glass-transition temperature (T_g) of the materials was around -50 °C (Figure 2b) when taken from the midpoint of the transition determined by differential scanning calorimetry (DSC) and around -35°C when obtained from the maximum of tan(δ) using dynamic mechanical analysis

(DMA) (Figure S4 and Table 1). The T_gs remained almost identical across the different materials independently from the varying crosslinking densities (*vide infra*).

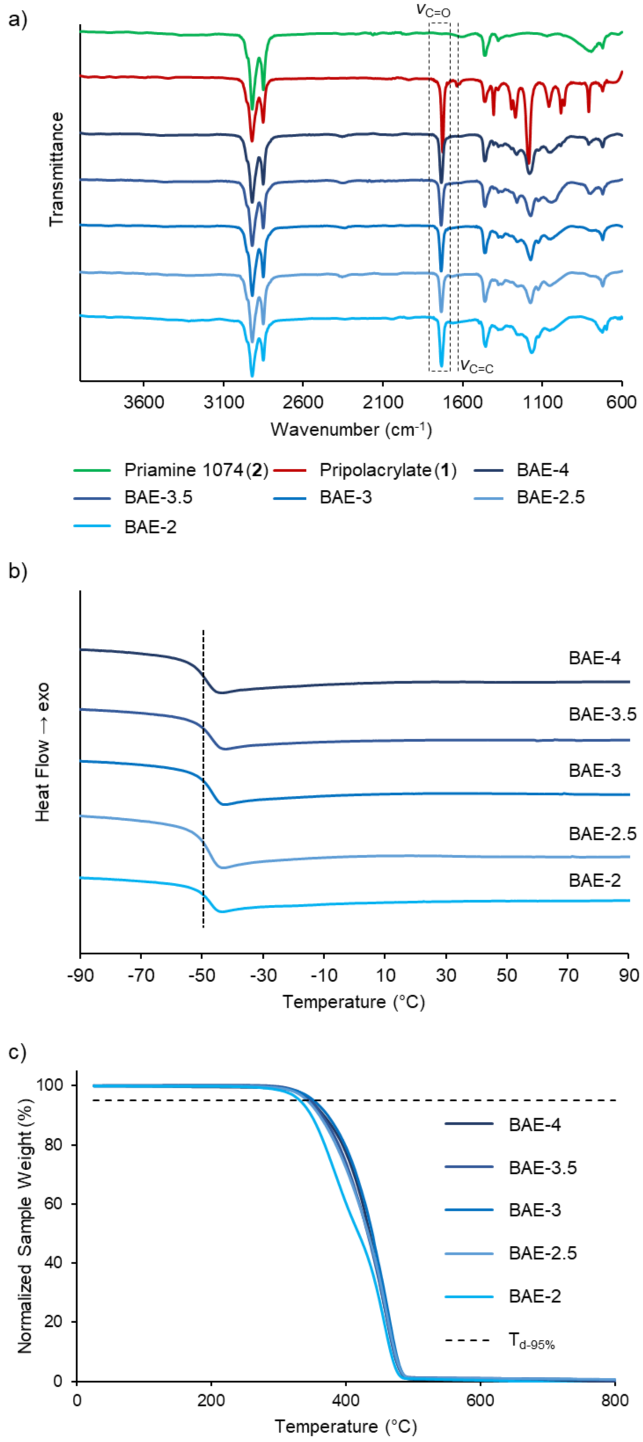


Figure 2. Material characterization. IR spectra of the monomers (**1** and **2**) and investigated polymer networks (a); DSC (b) and TGA (c) temperature ramp thermograms of polymer networks BAE-2 to BAE-4.

Thermogravimetric analyses (TGA) displayed onset degradation temperatures ($T_{d\text{-}95\%}$) in the range of 330−350 °C (Figure 2c and Table 1), which is well beyond the processing temperature and is confirming the high thermal stability of BAE-materials reported previously.[52]

Table 1. Overview of physical properties of *β*-amino ester-based CANs.

CAN	Equiv. ratio of monomer **(1) : (2)**	T_{gDSC} (°C)[a]	T_{gDMA} (°C)[b]	$T_{d\text{-}95\%}$ (°C)[c]	soluble fraction (%)[d]	swelling degree (%)[e]	$G'_{80°C}$ (MPa)[f]
BAE-2	1:1	-50	-37	330	22	790	0.074
BAE-2.5	1:0.875	-50	-36	345	5.3	320	0.447
BAE-3	1:0.75	-49	-36	350	1.6	220	1.00
BAE-3.5	1:0.625	-49	-34	345	1.9	180	1.62
BAE-4	1:0.5	-51	-34	345	2.8	200	1.64

[a] Glass transition temperature measured via DSC (T_{gDSC}). [b] Glass transition temperature measured via DMA (T_{gDMA}) and determined by the maximum of tanδ. [c] TGA onset temperatures after 5% weight loss ($T_{d\text{-}95\%}$). [d] Obtained after swelling for 5 days in THF and redrying. [e] Obtained after swelling in THF for 5 days at rt. [f] Storage modulus (G') taken from DMA measurements at 80°C.

Dynamic Properties of *β*-Amino Ester Materials. After assessing the thermal properties of the materials, a rheological characterization of the CANs was performed to investigate their dynamic material properties. In what follows, only the dynamic properties of BAE-2.5 to BAE-4 are discussed in detail, since the initial characterization (*vide supra*) clearly showed that BAE-2 is as expected only a loosely crosslinked, hyperbranched system and thus not a thermoset-like material.

Nevertheless, for the sake of completeness and to confirm this assumption, the characterization of BAE-2 can be found in the supporting information (Figures S4a, S6, S7a and Table S1).

Stress relaxation experiments were performed, showing that all tested materials exhibited stress-relaxation at 180°C, which is linked to the retro-aza-Michael reaction.[52,53] Full stress-relaxation data of each of the materials can be found in the supporting information (Figures S5-S6). A comparison of the obtained relaxation times for the different networks at 180°C showed an increase in relaxation times with higher crosslinking degrees from ~250 s for BAE-2.5 to 2200 s for BAE-4 (Figure 3a). The trend of slower stress-relaxation with increasing cross-linking density was already shown in other CAN-systems such as vinylogous urethane based vitrimers.[38] Overall, in stress-relaxation measurements with varying temperatures, a strong temperature dependence was observed that, when evaluated with an Arrhenius model, translated to activation energies of 117-216 kJ mol^{-1} (Figure S5-S6). It was previously reported that β-amino ester CANs exhibit remarkable creep resistance, yet smooth reprocessability, which can be attributed to this high temperature dependence.

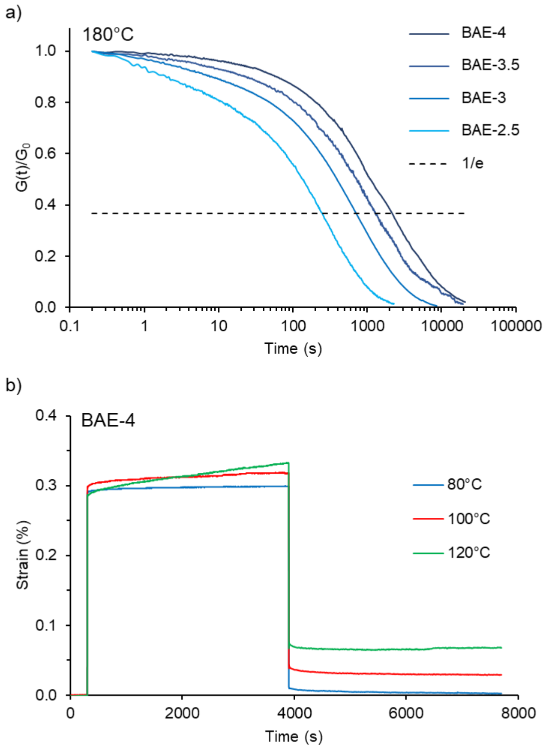


Figure 3. Comparison of relaxation times of the networks at 180°C (a) and exemplified elevated temperature creep behavior of BAE-4 (b).

Indeed, the herein investigated networks BAE-4 to BAE-2.5 show very low creep rates at elevated temperature upon application of 2 kPa shear stress for 60 minutes (Figure 3b, S7 and Table S1). In previous publications on creep resistant dynamic networks, the residual strain and/or the strain rate were used to evaluate their creep performance. However, reporting residual strain can be misleading because it is heavily dependent on the cross-linking density, applied stress, and measurement recovery time. Also, the determination of the "true" residual strain can be difficult in practice, since it is an asymptomatic value. In contrast, the creep rate ($\dot{\varepsilon}$) gives an indication on how fast permanent deformation will occur in the polymer network and moreover, the validity of this value can be easily checked by confirming that the strain deformation has entered the steady-state regime.[64] A more detailed theoretical description on this matter can be found in a previous publication from our group by Van Lijsebetten *et al.*.[65] While creep behavior of the BAE networks is thus discussed here using creep rates ($\dot{\varepsilon}$), the residual strain values are reported for sake of completeness in the supporting information (Table S2). In this context, the strong creep resistance of the crosslinked polymer networks (BAE-4 to BAE-2.5) is demonstrated by very low creep rates ($\dot{\varepsilon}$) at 80°C (~130°C above their T_g) in the range of zero measurable creep rate (BAE-4) to $5.0 \bullet 10^{-6}$ (%•s^{-1}) (BAE-2.5) and increases with decreasing crosslinking density. Even at higher temperatures the materials showed, especially for such elastomeric CANs, remarkably strong creep resistance with only very low creep rates of $5.0 \bullet 10^{-6}$ (100°C, BAE-4) to $5.0 \bullet 10^{-5}$ (%•s^{-1}) (Figure S7, Table S1). Such values are comparable to the creep rates of earlier reported creep resistant CANs, however at significantly higher temperatures above their respective T_g.[65]

Reprocessing. To demonstrate that the bio-based *β*-amino ester-based networks can be reprocessed several times while maintaining their material properties, BAE-3 was compression molded three times at 180°C and using 4 metric tons for 60 minutes, further referred to as R_0 for the virgin material and as R_1, R_2, and R_3 for the sample that is reprocessed 1, 2 or 3 times, respectively. The material showed excellent remolding ability after each cycle of cutting and remolding, yielding a fully transparent and homogenous plate (Figure S11). After each cycle, the thermal properties of the materials were assessed by DSC, TGA and chemical network structure by ATR-FTIR measurements (Figure S8). Additionally, samples R_0 and R_3 were subjected to rheological characterization in order to evaluate their stress-relaxation and creep characteristics (Figure 4, Figure S9, Figure S10 and Table S1).

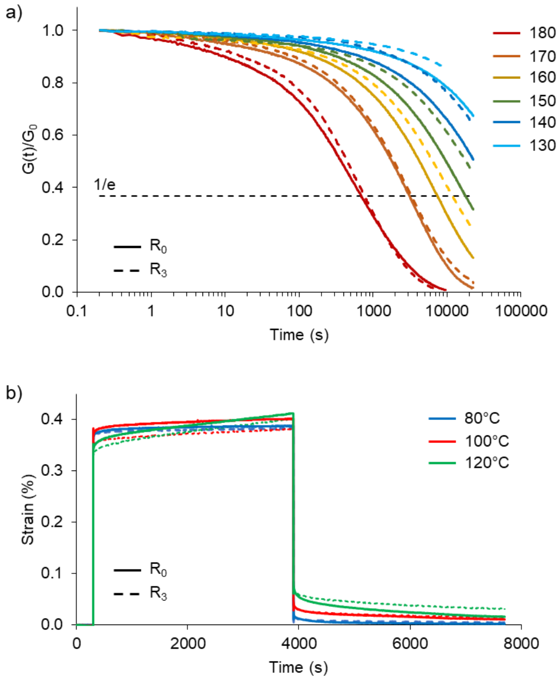


Figure 4. Comparison of stress relaxation (a) and creep measurements (b) of BAE-3 R_0 and R_3.

Infrared spectroscopy measurements of the material after each reprocessing cycle did not show any additional signals or intensity changes in the spectra, indicating no major changes in the chemical composition and thus network integrity of BAE-3 (Figure S8a). During DSC-analysis, a slight increase in the T_g from -49°C to -44°C was found (Figure S8b), while TGA-analysis showed that the thermal onset temperature remained high with a slight decrease from 350°C to 340°C (Figure S8c). The small change in T_g and $T_{deg5\%}$ is attributed to the dissociative exchange mechanism, which allows for side-reactions (amidation) or partly incomplete rearrangement of the acrylate and amine functionalities at high temperatures. Nevertheless, the overall properties of the network are maintained well after three reprocessing cycles.

In addition, when looking at the rheological properties, reprocessability of BAE-3 was further confirmed by stress-relaxation and creep measurements of R_0 and R_3 (Figure 4 and Figure S9-S10). The stress-relaxation measurements resulted in similar relaxation times at 180°C (705 s vs. 770 s) and 170°C (3130 s vs. 3380 s). Similar results were obtained by creep measurements after the performed reprocessing cycles. The determined creep rates remained below $5 \cdot 10^{-6}$ ($\%.s^{-1}$) and at similar levels before and after reprocessing at both 80°C and 100°C (Table S1). At 120°C, the determined creep rates displayed even the same values of $1.3 \cdot 10^{-5}$ ($\% \cdot s^{-1}$). Thus, the overall extremely low creep rates of the investigated CAN remain at a high level after reprocessing, underpinning the suitability of this chemistry platform for the creation of sustainable, creep resistant elastomers.

CONCLUSION

In this study, *ß*-amino ester containing CANs were made starting from fatty acid derived compounds (pripol and priamine), yielding around 90% bio-based carbon content. Besides their sustainable character, they also show promising material properties and extremely low creep rates, while still allowing reprocessing/recycling over multiple cycles and maintaining the material properties. The remarkable inherent suppressed creep of these rubbery materials, even at temperatures up to 120°C, should be highlighted as low creep resistance is usually considered a major drawback of CANs, limiting their industrial breakthrough.

The straightforward preparation of *ß*-amino ester-based CANs from a large variety of readily available (sustainable) building blocks by simply mixing acrylates and amines allows the design of a range of materials with tailored properties. This easy preparation, in combination with the inherent robustness, hydrolytic resistance, suppressed creep at elevated temperatures and the dynamic character of *β*-amino esters, makes the corresponding CANs quite promising for further application research in the area of sustainable and recyclable thermoset materials. For example, they could be implemented in applications ranging from coatings and adhesives up to bulk thermosetting materials.

ASSOCIATED CONTENT

The Supporting Information is available free of charge at XXXX showing additional NMR spectra, IR spectra, DSC, and TGA thermograms, stress relaxation data, creep, and DMA measurements.

AUTHOR INFORMATION

Corresponding Author

* Filip Du Prez, Polymer Chemistry Research group, Centre of Macromolecular Research (CMaC), Department of Organic and Macromolecular Chemistry, Ghent University, Krijgslaan 281 S4-bis, Ghent B-9000, Belgium; E-Mail: filip.duprez@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. ‡These authors contributed equally.

Funding Sources

This work was funded by BOF-UGent (GOA-funding). and the Research Foundation-Flanders (FWO)

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

FDP thanks BOF-UGent (GOA-funding). CT acknowledges the Research Foundation-Flanders (FWO) for the PhD fellowship (Grant 1S27920N). The authors would like to thank Bernhard De Meyer for the technical support and carrying out the DMA measurements. The authors would also like to thank Dr. Kevin De Bruycker for the stress relaxation data processing software and Dr. Nezha Badi, Dr. Chiel Mertens and Filip Van Lijsebetten for fruitful discussions.

REFERENCES

(1) Hopewell, J.; Dvorak, R.; Kosior, E. Plastics Recycling: Challenges and Opportunities. *Philos. Trans. R. Soc., B* **2009**, *364* (1526), 2115–2126. DOI: 10.1098/rstb.2008.0311

(2) PlasticsEurope. The Compelling Facts About Plastics 2007 An analysis of plastics production, demand and recovery for 2007 in Europe https://plasticseurope.org/wp-content/uploads/2021/10/2007-Compelling-facts.pdf (accessed 2022 -07 -13).

(3) Andrady, A. L.; Neal, M. A. Applications and Societal Benefits of Plastics. *Philos. Trans. R. Soc. B Biol. Sci.* **2009**, *364* (1526), 1977–1984. DOI: 10.1098/rstb.2008.0304

(4) Thompson, R. C.; Swan, S. H.; Moore, C. J.; Vom Saal, F. S. Our Plastic Age. *Philos. Trans. R. Soc. B Biol. Sci.* **2009**, *364* (1526), 1973–1976. DOI: 10.1098/rstb.2009.0054

(5) Thompson, R. C.; Moore, C. J.; Saal, F. S. V.; Swan, S. H. Plastics, the Environment and Human Health: Current Consensus and Future Trends. *Philos. Trans. R. Soc. B Biol. Sci.* **2009**, *364* (1526), 2153. DOI: 10.1098/rstb.2009.0053

(6) Horejs, C. Solutions to Plastic Pollution. *Nat. Rev. Mater.* **2020**, *5* (9), 641–641. DOI: 10.1038/s41578-020-00237-0

(7) Bentley, R. W. Global Oil & Gas Depletion: An Overview. *Energy Policy* **2002**, *30* (3), 189–205. DOI: 10.1016/S0301-4215(01)00144-6

(8) Patrick, J. F.; Robb, M. J.; Sottos, N. R.; Moore, J. S.; White, S. R. Polymers with Autonomous Life-Cycle Control. *Nature* **2016**, *540* (7633), 363–370. DOI: 10.1038/nature21002

(9) Fortman, D. J.; Brutman, J. P.; De Hoe, G. X.; Snyder, R. L.; Dichtel, W. R.; Hillmyer, M. A. Approaches to Sustainable and Continually Recyclable Cross-Linked Polymers. *ACS Sustain. Chem. Eng.* **2018**, *6* (9), 11145–11159. DOI: 10.1021/acssuschemeng.8b02355

(10) Gandini, A.; Lacerda, T. M. From Monomers to Polymers from Renewable Resources: Recent Advances. *Prog. Polym. Sci.* **2015**, *48*, 1–39. DOI: 10.1016/j.progpolymsci.2014.11.002

(11) Ma, S.; Webster, D. C. Naturally Occurring Acids as Cross-Linkers To Yield VOC-Free, High-Performance, Fully Bio-Based, Degradable Thermosets. *Macromolecules* **2015**, *48* (19), 7127–7137. DOI: 10.1021/acs.macromol.5b01923

(12) Türünç, O.; Billiet, S.; De Bruycker, K.; Ouardad, S.; Winne, J.; Du Prez, F. E. From Plant Oils to Plant Foils: Straightforward Functionalization and Crosslinking of Natural Plant Oils with Triazolinediones. *Eur. Polym. J.* **2015**, *65*, 286–297. DOI: 10.1016/j.eurpolymj.2014.12.013

(13) Caillol, S.; Boutevin, B.; Auvergne, R. Eugenol, a Developing Asset in Biobased Epoxy Resins. *Polymer* **2021**, *223*, 123663. DOI: 10.1016/j.polymer.2021.123663

(14) Faye, I.; Decostanzi, M.; Ecochard, Y.; Caillol, S. Eugenol Bio-Based Epoxy Thermosets: From Cloves to Applied Materials. *Green Chem.* **2017**, *19* (21), 5236–5242. DOI: 10.1039/C7GC02322G

(15) Zhao, S.; Abu-Omar, M. M. Biobased Epoxy Nanocomposites Derived from Lignin-Based

Monomers. *Biomacromolecules* **2015**, *16* (7), 2025–2031. DOI: 10.1021/acs.biomac.5b00670

(16) Mora, A. S.; Tayouo, R.; Boutevin, B.; David, G.; Caillol, S. Vanillin-Derived Amines for Bio-Based Thermosets. *Green Chem.* **2018**, *20* (17), 4075–4084. DOI: 10.1039/C8GC02006J

(17) Hong, J.; Radojčić, D.; Ionescu, M.; Petrović, Z. S.; Eastwood, E. Advanced Materials from Corn: Isosorbide-Based Epoxy Resins. *Polym. Chem.* **2014**, *5* (18), 5360–5368. DOI: 10.1039/C4PY00514G

(18) Zou, W.; Dong, J.; Luo, Y.; Zhao, Q.; Xie, T. Dynamic Covalent Polymer Networks: From Old Chemistry to Modern Day Innovations. *Adv. Mater.* **2017**, *29* (14), 1606100. DOI: 10.1002/adma.201606100

(19) Scott, T. F.; Schneider, A. D.; Cook, W. D.; Bowman, C. N. Photoinduced Plasticity in Cross-Linked Polymers. *Science* **2005**, *308* (5728), 1615–1617. DOI: 10.1126/science.1110505

(20) Chen, X.; Dam, M. A.; Ono, K.; Mal, A.; Shen, H.; Nutt, S. R.; Sheran, K.; Wudl, F. A Thermally Re-Mendable Cross-Linked Polymeric Material. *Science* **2002**, *295* (5560), 1698–1702. DOI: 10.1126/science.1065879

(21) Podgórski, M.; Fairbanks, B. D.; Kirkpatrick, B. E.; McBride, M.; Martinez, A.; Dobson, A.; Bongiardina, N. J.; Bowman, C. N. Toward Stimuli-Responsive Dynamic Thermosets through Continuous Development and Improvements in Covalent Adaptable Networks (CANs). *Adv. Mater.* **2020**, *32* (20), 1906876. DOI: 10.1002/adma.201906876

(22) Tobolsky, A. V.; Prettyman, I. B.; Dillon, J. H. Stress Relaxation of Natural and Synthetic Rubber Stocks. *Rubber Chem. Technol.* **1944**, *17* (3), 551–575. DOI: 10.1063/1.1707442

(23) Osthoff, R. C.; Bueche, A. M.; Grubb, W. T. Chemical Stress-Relaxation of Polydimethylsiloxane Elastomers. *J. Am. Chem. Soc.* **1954**, *76* (18), 4659–4663. DOI: 10.1021/ja01647a052

(24) Zheng, P.; McCarthy, T. J. A Surprise from 1954: Siloxane Equilibration Is a Simple, Robust, and Obvious Polymer Self-Healing Mechanism. *J. Am. Chem. Soc.* **2012**, *134* (4), 2024–2027. DOI: 10.1021/ja2113257

(25) Stern, M. D.; Tobolsky, A. V. Stress-Time-Temperature Relations in Polysulfide Rubbers. *Rubber Chem. Technol.* **1946**, *19* (4), 1178–1192. DOI: 10.5254/1.3543255

(26) McBride, M. K.; Worrell, B. T.; Brown, T.; Cox, L. M.; Sowan, N.; Wang, C.; Podgorski, M.; Martinez, A. M.; Bowman, C. N. Enabling Applications of Covalent Adaptable Networks. *Annu. Rev. Chem. Biomol. Eng.* **2019**, *10*, 175–198. DOI: 10.1146/annurev-chembioeng-060718-030217

(27) Bowman, C. N.; Kloxin, C. J. Covalent Adaptable Networks: Reversible Bond Structures Incorporated in Polymer Networks. *Angew. Chemie Int. Ed.* **2012**, *51* (18), 4272–4274. DOI: 10.1002/anie.201200708

(28) Lei, Z. Q.; Xiang, H. P.; Yuan, Y. J.; Rong, M. Z.; Zhang, M. Q. Room-Temperature Self-Healable and Remoldable Cross-Linked Polymer Based on the Dynamic Exchange of Disulfide Bonds. *Chem. Mater.* **2014**, *26* (6), 2038–2046. DOI: 10.1021/cm4040616

(29) Rekondo, A.; Martin, R.; Ruiz De Luzuriaga, A.; Cabañero, G.; Grande, H. J.; Odriozola, I. Catalyst-Free Room-Temperature Self-Healing Elastomers Based on Aromatic Disulfide Metathesis. *Mater. Horizons* **2014**, *1* (2), 237–240. DOI: 10.1039/C3MH00061C

(30) 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. DOI: 10.1021/acsmacrolett.8b00667

(31) Tretbar, C. A.; Neal, J. A.; Guan, Z. Direct Silyl Ether Metathesis for Vitrimers with Exceptional Thermal Stability. *J. Am. Chem. Soc.* **2019**, *141* (42), 16595–16599. DOI: 10.1021/jacs.9b08876

(32) Nishimura, Y.; Chung, J.; Muradyan, H.; Guan, Z. Silyl Ether as a Robust and Thermally Stable Dynamic Covalent Motif for Malleable Polymer Design. *J. Am. Chem. Soc.* **2017**, *139* (42), 14881–14884. DOI: 10.1021/jacs.7b08826

(33) Montarnal, D.; Capelot, M.; Tournilhac, F.; Leibler, L. Silica-like Malleable Materials from Permanent Organic Networks. *Science* **2011**, *334* (6058), 965–968. DOI: 10.1126/science.1212648

(34) Capelot, M.; Montarnal, D.; Tournilhac, F.; Leibler, L. Metal-Catalyzed Transesterification for Healing and Assembling of Thermosets. *J. Am. Chem. Soc.* **2012**, *134* (18), 7664–7667. DOI: 10.1021/ja302894k

(35) Wang, C.; Goldman, T. M.; Worrell, B. T.; McBride, M. K.; Alim, M. D.; Bowman, C. N. Recyclable and Repolymerizable Thiol–X Photopolymers. *Mater. Horizons* **2018**, *5* (6), 1042–1046. DOI: 10.1039/C8MH00724A

(36) Delahaye, M.; Winne, J. M.; Du Prez, F. E. Internal Catalysis in Covalent Adaptable Networks: Phthalate Monoester Transesterification As a Versatile Dynamic Cross-Linking Chemistry. *J. Am. Chem. Soc.* **2019**, *141* (38), 15277–15287. DOI: 10.1021/jacs.9b07269

(37) Van Lijsebetten, F.; Spiesschaert, Y.; Winne, J. M.; Du Prez, F. E. Reprocessing of Covalent Adaptable Polyamide Networks through Internal Catalysis and Ring-Size Effects. *J. Am. Chem. Soc.* **2021**, *143* (38), 15834–15844. DOI: 10.1021/jacs.1c07360

(38) Spiesschaert, Y.; Taplan, C.; Stricker, L.; Guerre, M.; Winne, J. M.; Du Prez, F. E. Influence of the Polymer Matrix on the Viscoelastic Behaviour of Vitrimers. *Polym. Chem.* **2020**, *11* (33), 5377–5385. DOI: 10.1039/D0PY00114G

(39) Denissen, W.; Rivero, G.; Nicolaÿ, R.; Leibler, L.; Winne, J. M.; Du Prez, F. E. Vinylogous Urethane Vitrimers. *Adv. Funct. Mater.* **2015**, *25* (16), 2451–2457. DOI: 10.1002/adfm.201404553

(40) Taplan, C.; Guerre, M.; Bowman, C. N.; Du Prez, F. E. Surface Modification of (Non)-Fluorinated Vitrimers through Dynamic Transamination. *Macromol. Rapid Commun.* **2021**, *42* (7), 2000644. DOI: 10.1002/marc.202000644

(41) Hendriks, B.; Waelkens, J.; Winne, J. M.; Du Prez, F. E. Poly(Thioether) Vitrimers via Transalkylation of Trialkylsulfonium Salts. *ACS Macro Lett.* **2017**, *6* (9), 930–934. DOI: 10.1021/acsmacrolett.7b00494

(42) Obadia, M. M.; Mudraboyina, B. P.; Serghei, A.; Montarnal, D.; Drockenmuller, E. Reprocessing and Recycling of Highly Cross-Linked Ion-Conducting Networks through Transalkylation Exchanges of C-N Bonds. *J. Am. Chem. Soc.* **2015**, *137* (18), 6078–6083. DOI: 10.1021/jacs.5b02653

(43) Anaya, O.; Jourdain, A.; Antoniuk, I.; Ben Romdhane, H.; Montarnal, D.; Drockenmuller, E. Tuning the Viscosity Profiles of High-Tg Poly(1,2,3-Triazolium) Covalent Adaptable Networks by the Chemical Structure of the N-Substituents. *Macromolecules* **2021**, *54* (7), 3281–3292. DOI: 10.1021/acs.macromol.0c02221

(44) Chapelle, C.; Quienne, B.; Bonneaud, C.; David, G.; Caillol, S. Diels-Alder-Chitosan Based Dissociative Covalent Adaptable Networks. *Carbohydr. Polym.* **2021**, *253*, 117222. DOI: 10.1016/j.carbpol.2020.117222

(45) 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. DOI: 10.1021/jacs.5b08084

(46) Lu, Y. X.; Tournilhac, F.; Leibler, L.; Guan, Z. Making Insoluble Polymer Networks Malleable via Olefin Metathesis. *J. Am. Chem. Soc.* **2012**, *134* (20), 8424–8427. DOI: 10.1021/ja303356z

(47) Röttger, M.; Domenech, T.; Van Der Weegen, R.; Breuillac, A.; Nicolaÿ, R.; Leibler, L. High-Performance Vitrimers from Commodity Thermoplastics through Dioxaborolane Metathesis. *Science* **2017**, *356* (6333), 62–65. DOI: 10.1126/science.aah5281

(48) 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* **2020**, *132* (9), 3637–3646. DOI: 10.1002/anie.201912902

(49) Elling, B. R.; Dichtel, W. R. Reprocessable Cross-Linked Polymer Networks: Are Associative Exchange Mechanisms Desirable? *ACS Cent. Sci.* **2020**, *6* (9), 1488–1496. DOI: 10.1021/acscentsci.0c00567

(50) 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. DOI: 10.1039/C9PY01260E

(51) Van Zee, N. J.; Nicolaÿ, R. Vitrimers: Permanently Crosslinked Polymers with Dynamic Network Topology. *Prog. Polym. Sci.* **2020**, *104*, 101233. DOI: 10.1016/j.progpolymsci.2020.101233

(52) Taplan, C.; Guerre, M.; Du Prez, F. E. Covalent Adaptable Networks Using β-Amino Esters as Thermally Reversible Building Blocks. *J. Am. Chem. Soc.* **2021**, *143* (24), 9140–9150. DOI: 10.1021/jacs.1c03316

(53) Holloway, J. O.; Taplan, C.; Du Prez, F. E. Combining Vinylogous Urethane and β-Amino Ester Chemistry for Dynamic Material Design. *Polym. Chem.* **2022**, *13* (14), 2008–2018. DOI: 10.1039/D2PY00026A

(54) Berne, D.; Coste, G.; Morales-Cerrada, R.; Boursier, M.; Pinaud, J.; Ladmiral, V.; Caillol, S. Taking Advantage of β-Hydroxy Amine Enhanced Reactivity and Functionality for the Synthesis of Dual Covalent Adaptable Networks. *Polym. Chem.* **2022**, *13* (25), 3806–3814. DOI: 10.1039/D2PY00274D

(55) Zhang, H.; Bré, L. P.; Zhao, T.; Zheng, Y.; Newland, B.; Wang, W. Mussel-Inspired Hyperbranched Poly(Amino Ester) Polymer as Strong Wet Tissue Adhesive. *Biomaterials* **2014**, *35* (2), 711–719. DOI: 10.1016/j.biomaterials.2013.10.017

(56) González, G.; Fernández-Francos, X.; Serra, À.; Sangermano, M.; Ramis, X. Environmentally-Friendly Processing of Thermosets by Two-Stage Sequential Aza-Michael Addition and Free-Radical Polymerization of Amine–Acrylate Mixtures. *Polym. Chem.* **2015**, *6* (39), 6987–6997. DOI: 10.1039/c5py00906e

(57) Zhao, S.; Wang, D.; Russell, T. P. Biobased Dynamic Polymer Networks with Rapid Stress Relaxation. *ACS Sustain. Chem. Eng.* **2021**, *9* (33), 11091–11099. DOI: 10.1021/acssuschemeng.1c02826

(58) Dhers, S.; Vantomme, G.; Avérous, L. A Fully Bio-Based Polyimine Vitrimer Derived from Fructose. *Green Chem.* **2019**, *21* (7), 1596–1601. DOI: 10.1039/C9GC00540D

(59) Engelen, S.; Wróblewska, A. A.; De Bruycker, K.; Aksakal, R.; Ladmiral, V.; Caillol, S.; Du Prez, F. E. Sustainable Design of Vanillin-Based Vitrimers Using Vinylogous Urethane Chemistry. *Polym. Chem.* **2022**, *13* (18), 2665–2673. DOI: 10.1039/D2PY00351A

(60) Lucherelli, M. A.; Duval, A.; Avérous, L. Biobased Vitrimers: Towards Sustainable and Adaptable Performing Polymer Materials. *Prog. Polym. Sci.* **2022**, *127*, 101515. DOI: 10.1016/j.progpolymsci.2022.101515

(61) Droesbeke, M. A.; Du Prez, F. E. Sustainable Synthesis of Renewable Terpenoid-Based (Meth)Acrylates Using the CHEM21 Green Metrics Toolkit. *ACS Sustain. Chem. Eng.* **2019**, *7* (13), 11633–11639. DOI: 10.1021/acssuschemeng.9b01578

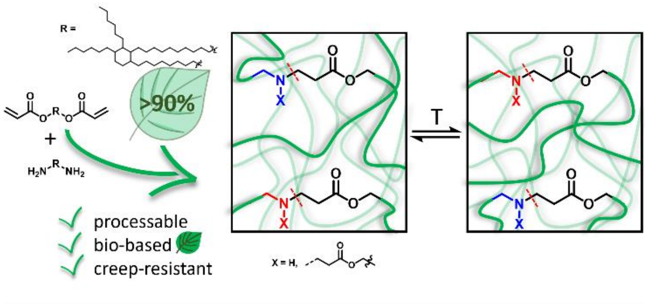
(62) Veith, C.; Diot-Néant, F.; Miller, S. A.; Allais, F. Synthesis and Polymerization of Bio-Based Acrylates: A Review. *Polym. Chem.* **2020**, *11* (47), 7452–7470. DOI: 10.1039/D0PY01222J

(63) Bonnotte, T.; Paul, S.; Araque, M.; Wojcieszak, R.; Dumeignil, F.; Katryniok, B. Dehydration of Lactic Acid: The State of The Art. *ChemBioEng Rev.* **2018**, *5* (1), 34–56. DOI: 10.1002/cben.201700012

(64) Münstedt, H. Rheological Experiments at Constant Stress as Efficient Method to Characterize Polymeric Materials. *J. Rheol. (N. Y. N. Y).* **2014**, *58* (3), 565–587. DOI: 10.1122/1.4866049

(65) Lijsebetten, F. Van; Bruycker, K. De; Spiesschaert, Y.; Winne, J. M.; Prez, F. E. Du. Suppressing Creep and Promoting Fast Reprocessing of Vitrimers with Reversibly Trapped Amines. *Angew. Chemie* **2022**, *134* (9), e202113872. DOI: 10.1002/anie.202113872

For Table of Contents Use Only



Synopsis:

Elastomeric covalent adaptable networks with more than 90% bio-renewable carbon exhibit remarkably low creep rates, even at elevated temperatures.