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Covalent Adaptable Networks Using β -Amino Esters as Thermally Reversible Building Blocks

Christian Taplan, Marc Guerre, and Filip E. Du Prez*

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ABSTRACT: In this study, β -amino esters, prepared by the aza-Michael addition of an amine to an acrylate moiety, are investigated as building blocks for the formation of dynamic covalent networks. While such amino esters are usually considered as thermally nondynamic adducts, the kinetic model studies presented here show that dynamic covalent exchange occurs via both dynamic aza-Michael reaction and catalyst-free transesterification. This knowledge is transferred to create β -amino esterbased covalent adaptable networks (CANs) with coexisting dissociative and associative covalent dynamic exchange reactions. The ease, robustness, and versatility of this chemistry are demonstrated by using a variety of readily available multifunctional acrylates and amines. The presented CANs are reprocessed via



either a dynamic aza-Michael reaction or a catalyst-free transesterification in the presence of hydroxyl moieties. This results in reprocessable, densely cross-linked materials with a glass transition temperature (T_g) ranging from -60 to 90 °C. Moreover, even for the low T_g materials, a high creep resistance was demonstrated at elevated temperatures up to 80 °C. When additional β -hydroxyl group-containing building blocks are applied during the network design, an enhanced neighboring group participation effect allows reprocessing of materials up to 10 times at 150 °C within 30 min while maintaining their material properties.

■ INTRODUCTION

Current times are often referred to as the plastic era in which a life without polymer materials is unimaginable. However, plastic pollution accompanying the technological advancements is becoming an ever increasing issue.^{1,2} In particular, one important polymer material category, referred to as thermosetting materials, which was intentionally designed to be dimensionally stable and to provide high chemical and mechanical durability, is nowadays in the focus of research toward sustainable end-of-life options. Indeed, despite their superior properties compared to thermoplastics, thermosets are very challenging to recycle and consequently often simply go to waste or are being incinerated.³ Therefore, the scientific community proposed strategies to implement reversible covalent bonds into the thermoset compositions, which allowed the creation of three-dimensional covalent networks, yet with reversible cross-linking points making reprocessing upon a stimulus possible.4-

The introduction of covalent adaptable networks (CANs) followed a tradition in science and chemistry to consider molecules and reactions from the past as inspiration to solve current problems and push scientific boundaries.⁷ In fact, already decades ago, it was reported that cross-linked rubbers using disulfide bonds and silyl ethers showed thermally activated dynamic behavior and thus enabled the creation of reprocessable covalent networks.^{8–11} In more recent years,

scientists put much research effort in exploring additional covalent dynamic reactions.^{12–14} For CANs, applicable dynamic covalent reactions are for instance reversible cyclo-additions,^{4,15,16} disulfide^{17–20} or silyl ether exchange,^{21,22} transalkylation,^{23–25} trans(thio)esterification,^{6,26,27} transamina-tion^{28–33} of various reactive centers, and others.^{34–39}

Many of those chemistry platforms have also been highlighted in recent reviews.^{40–44} Some of them apply concepts of internal catalysis or neighboring group participation (NGP) to accelerate or enable exchange in the first place.⁴⁵ This was for instance applied in the context of the aforementioned silyl ether exchange by using a γ -positioned amino moiety²¹ and also, for transesterifications, by leveraging a β -hydroxyl group.⁶ Also, introducing a carboxylic or a sulfonic acid group in proximity of an ester group was found to promote a dissociative transesterification mechanism when terephthalate esters were applied.^{46,47} Modifying the nucleophile in the exchange reaction by making using of β -amino

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Two coexisting mechanistic pathways were reported when thiols were used to create thioesters, i.e., an associative and dissociative one.⁴⁹ Other chemical reactions allow for two coexisting mechanistic pathways,²⁸ making use of different exchange chemistries separately,⁵⁰ adjusting the dissociation rate with varying substituents,⁵¹ or combining dissociative with associative exchange reactions elegantly using thiols.^{52,53} Yet combining associative and dissociative dynamic covalent chemistries in a straightforward fashion is rather rare. Recently, Dichtel and Elling raised the question of whether the use of a solely associative exchange mechanism is desirable in view of material design constraints to meet current processing challenges.⁵⁴

In this context, here a strategy is presented based on the aza-Michael addition of amines to acrylates (Scheme 1). First, the

Scheme 1. Display of an Aza-Michael Addition between Amines and Acrylates with the Formation of a β -Amino Ester That Provides Possibilities for Associative and Dissociative Covalent Dynamic Chemistries



created activated esters promote catalyst-free transesterification with alcohol groups as associative exchange mechanism, with the advantage of maintaining cross-linking points and a gradual decrease in viscosity. In addition, the formed aza-Michael adducts allow for a reversible, dissociative breaking point on the electrophilic side of the dynamic unit. Moreover, possible side reactions, originating from, e.g., amidation reactions, are not expected to harm the reprocessability of the network, since an acrylamide is expected to be more prone to undergo reversible aza-Michael reaction and the released alcohol is available for transesterification. All of this is achieved in a straightforward fashion and thus provides an opportunity to use a myriad of readily available acrylate, amine, and alcohol functionalities.

The aza-Michael reaction was widely explored and studied in the context of biomaterials and investigated as for instance degradable polymer materials, for gene delivery, or as precursors for thermosetting resins.^{55–59} Yet interestingly, apart from applying a specifically designed cross-linker,⁶⁰ the aza-Michael reaction is usually considered to create permanent bonds in bulk materials and was applied for creating permanently cross-linked reference materials.⁶¹ Hence, to the best of our knowledge, β -amino esters were not explored in CANs despite their vast application potential.

RESULTS

Model Reactions of β **-Amino Esters.** The first research question was to investigate whether a β -amino ester can undergo thermally activated dynamic covalent exchange and by which mechanisms this could occur. For this purpose, *N*-methylbutylamine was reacted with 2-ethylhexyl acrylate to form 2-ethylhexyl 3-(butyl(methyl)amino)propanoate (1) (Figure 1 and Figure S1). This model compound 1 was



Figure 1. (a) Reaction scheme describing the catalyst-free dynamic exchange with (i) the transesterification of the β -amino ester **1** with benzyl alcohol and (ii) the dynamic (retro) aza-Michael reaction with benzyl acrylate. (b) Arrhenius plots of the monitored reactions obtained by following the decay of **1** as a function of time at each of the investigated temperatures.

obtained with a 95% yield after purification. Afterward, kinetic experiments were conducted in bulk at various temperatures in the presence of an excess of either benzyl alcohol or benzyl acrylate to check for transesterification or dynamic aza-Michael reaction, respectively (Figure 1). This excess allowed us to push the system kinetically to a pseudo-first-order reaction so that linearity during the first time points, from which the reaction constants are obtained, was maintained.

When monitoring thermally activated transesterification, the β -amino ester 1 was combined with 12 equiv of benzyl alcohol (reaction 1 in Figure 1a). This reaction was monitored via ¹H NMR by following the disappearance of the signal at 3.91 ppm belonging to 1 and the appearance of the signal at 3.42 ppm attributed to the newly formed 2-ethylhexyl alcohol. NMR spectra corresponding to the kinetic study at 100 °C are provided in the Supporting Information (Figure S2). Notably, the reappearance of the proton signals between 5.70 and 6.30 ppm, corresponding to the acrylate of the respective amino

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CAN	acrylate	amine	T_{gDSC}^{a} (°C)	$T_{d-95\%}^{b}$ (°C)	soluble fraction c (%)	swelling degree ^d (%)	$E_{\rm a(flow)}~({\rm kJ~mol^{-1}})$	$G^{\prime f}\left(\mathrm{MPa} ight)$
BAE-1	TMPTA	Jeffamine	-57	315	15	455	163 ± 12	0.45 ± 0.05
BAE-2	TMPTA	Priamine	-13	275	3.0	85	170 ± 14	0.96 ± 0.01
BAE-3	TMPTA	MBCA	62	280	е	45	153 ± 6	1.38 ± 0.02
BAE-1-OH	PTA	Jeffamine	-59	330	5.8	295	242 ± 8	0.72 ± 0.01
BAE-2-OH	PTA	Priamine	-2	300	2.4	65	110 ± 4	1.16 ± 0.01
BAE-3-OH	PTA	MBCA	93	295	е	15	184 ± 7	0.89 ± 0.05
^a DSC glass tra	nsition tem	perature (T_{q})	osc). ^b TGA on	set temperatur	es after 5% weight loss	s $(T_{d_{2}95\%})$. ^c Obtained a	ufter Soxhlet extracti	on for 24 h in

THF. Obtained after swelling in THF for 7 days at rt. No soluble fraction detectable. fObtained from a time sweep measurement at 120 °C.

ester, is detected and pointing to a thermally reversible behavior of the aza-Michael-adduct (*vide infra*). Monitoring different temperatures, ranging from 80 to 140 °C, resulted in a kinetic plot that demonstrates the possibility for the β -amino ester 1 to undergo thermally activated, catalyst-free transesterification (Figure 1b and Figure S4a).

Furthermore, because 1 provides a tertiary amine and upon dissociation also a secondary amino moiety, for which a catalytic effect was earlier described to catalyze the transesterification for epoxy networks,⁶² the transesterification of 1 was tested in the presence of either a tertiary or a secondary amine as external catalyst. Therefore, 5 mol % of N_iN -diisopropylethylamine (DIPEA) or dibutylamine was added to the reaction mixture and the reaction was monitored at 120 °C. The obtained reaction rates were not found to be strikingly different in the presence of these catalysts, thus not justifying the use of an external catalyst (Figure S3).

Since the appearance of the acrylate signals was detected at 100 °C in the original model study, in a next step the possibility for the β -amino ester 1 to undergo a dynamic aza-Michael reaction was investigated in a temperature window from 100 to 160 °C (Figure S5). In order to target the same exchange reaction product 2, the reaction was conducted with benzyl acrylate. Yet, to avoid the influence of the acrylates' homopolymerization at such elevated temperatures, the amount of benzyl acrylate was decreased to 6 equiv. In the monitored temperature window, the exchange rate to form β amino ester 2 appeared to be slower than via the transesterification mechanism (Figure 1b and Figure S4b). This slow exchange rate of the aza-Michael reaction might be explained by the stability of the adduct, originating from the addition of an amine to an acrylate. At lower temperatures, the readily formed adduct is favored; hence dynamic exchange is unlikely, while at increased temperatures the equilibrium of the (retro) aza-Michael reaction is shifted to the dissociated state, as expected for an addition-elimination type of dynamic covalent exchange reactions.⁴⁴ However, the exchange via the dynamic aza-Michael reaction follows a higher temperature dependency, as also expressed by the activation energies of 35 \pm 2 kJ mol⁻¹ and 75 \pm 6 kJ mol⁻¹ calculated for the monitored transesterification and dynamic aza-Michael reaction, respectively (Figure 1b). Interestingly, while the exchange rates are very slow at 100 °C, they become moderately high at higher temperatures with a strong temperature dependence as shown with an Arrhenius plot. The fact that β -amino esters undergo dynamic bond exchanges at elevated temperatures, via both an associative and dissociative dynamic bond exchange, was intriguing and unique in the context of CANs (vide infra) as this would allow for potential coexistence of both mechanisms at material processing temperatures.

β-Amino Esters-Based Covalent Adaptable Networks. This conceptually demonstrated catalyst-free dynamic covalent exchange chemistry was translated to the design of CANs. Therefore, several β-amino ester-based networks (BAE) were synthesized via the aza-Michael addition of small and macromolecular multifunctional primary amines (4,4'-methylenebis(cyclohexylamine) (MBCA), Jeffamine D2000, and Priamine 1074) with two types of multifunctional, technical grade acrylates (trimethylolpropane triacrylate (TMPTA) and pentaerythritol triacrylate (PTA)) for which the radical stabilizer was not removed (Table 1).

PTA provided additional hydroxyl groups, which allowed the investigation of the BAEs with or without pendent OH-groups (referred to as BAE-X-OH and BAE-X, respectively). Network synthesis was conducted in bulk, targeting stoichiometric amounts of amine protons to acrylates (Figure 2a).



Figure 2. (a) Reaction scheme of the formation of β -amino ester networks. (b) A reprocessed TMPTA/Jeffamine D2000 (BAE-1) sample, leveraging the retro aza-Michael reaction as covalent dynamic chemistry.

The mixtures were cured at 70 °C for 72 h for Jeffamine D2000 (BAE-1, BAE-1-OH) and 48 h for Priamine 1074 (BAE-2, BAE-2-OH) and MBCA (BAE-3, BAE-3-OH) containing networks (Table 1). The conversion was checked via ATR-FTIR (Figure S6) and network formation verified via swelling tests and Soxhlet extraction with THF (Table 1). Swelling ratios in THF increased when lowering the cross-linking density and ranged from 455% (BAE-1) to 15% (BAE-3-OH). As expected, when considering hydrogen bonding, the additional hydroxyl groups in PTA-based CANs consistently resulted in lower swelling degrees. In addition, even for Jeffamine-based materials showing high swelling ratios, relatively low soluble fractions were obtained. Moreover, no soluble fraction was detected for BAE-3 and BAE-3-OH, which is ascribed to the high cross-linking density of these materials.

Time sweep experiments were performed at 120 °C to limit the influence of a dissociation process that is linked to a retro aza-Michael reaction (*vide infra*). The elastic shear modulus (*G'*, Table 1), associated with the cross-link density, follows the same trend as obtained from the swelling degree and T_g (Figure S7). The only apparent exception to this trend is the lower *G'*-value for BAE-3-OH in comparison to the Priamine cross-linked network (BAE-2-OH) and to the TMPTA crosslinked reference materials (BAE-3). This is ascribed to the fact that the temperature difference between the T_g of BAE-3-OH (93 °C) and the temperature chosen for the rheological experiments (120 °C) is much smaller than for the other materials.

Each of these polymer networks was used to demonstrate the possibility of creating thermally reprocessable cross-linked materials on the basis of both catalyst-free dynamic transesterification and dynamic aza-Michael reaction. Hence, they were compression molded into a plate, exemplified for BAE-1 (Figure 2b) and BAE-3 (Figure S8) at 180 °C, a temperature well below the degradation temperature, within 1 h and with an applied pressure of 2–4 tons. A reference network, obtained by UV-cured pentaerythritol triacrylate in the absence of β amino esters, was not reprocessable, even after 2 h of hot pressing at 180 °C (Figure S9) and was therefore not suitable for stress relaxation measurements.

The reprocessable materials displayed T_g values from -60 to 90 °C, as measured by differential scanning calorimetry (DSC) (Table 1 and Figure S10). It should be noted that PTA based CANs displayed a higher T_g than their non-hydroxyl group containing counterpart CANs based on TMPTA, as expected from the additional hydrogen bond interactions. TGA-analysis displayed a degradation onset temperature ($T_{d-95\%}$) in a range of 275-330 °C (Table 1, Figure S11), well beyond the processing temperature. Besides, the multifunctional amine compounds with a boiling point beyond processing temperatures are expected to remain part of the network. This is exemplified with BAE-3-OH ($T_{d-95\%}$ = 295 °C), in which the isothermal mass loss was determined to be less than 1.5% weight loss after 1 h at 200 °C (Figure 3, black line).

Moreover, when low molecular mass primary amines, i.e., butylamine, octylamine, and 2-ethylhexylamine, were used as reaction partner (with stoichiometric amounts of amine protons to acrylates) to form dynamic β -amino ester networks, they did not only show an earlier onset temperature in a TGA temperature ramp (Figure 3a,b) but also demonstrated a dramatically higher amount of mass loss under similar isothermal conditions (Figure 3c). This observation confirms



Figure 3. (a) Aza-Michael-based polymer networks originating from PTA and different amines. (b) TGA showing an earlier onset temperature after 5% wt loss between 230 and 240 °C for butyl-, octyl-, and 2-ethylhexylamine in comparison to the less volatile 4,4'methylenebis(cyclohexylamine) (295 °C). (c) Representation of the weight loss versus time of the polymer networks under isothermal conditions at 200 °C in the course of 1 h.

the retro aza-Michael reaction occurring in such bulk materials, as demonstrated in the model study described above.

Dynamic Properties of β -Amino Ester Based Materials. Rheological characterization of the created CANs was performed to investigate the dynamic material properties. First, when stress relaxation experiments were performed, it was observed that each of the networks displayed stress relaxation at 180 °C (Figures S12–S15). Additionally, a higher exchange rate (linked to faster stress relaxation) was detected when a hydroxyl group bearing acrylate (i.e., PTA) was used compared to TMPTA in elastomeric materials. As even in similar systems⁶³ differences in, for example, cross-link density or polarity were reported to influence the dynamic exchange, including variation of the flow activation energy, the applied variations among the materials make it difficult to describe a

trend at this stage. Nonetheless, in the herein presented system, dynamic aza-Michael and transesterification were concurrently occurring at elevated temperatures, and elastomeric materials with pendent hydroxyl groups displayed a faster exchange rate, as exemplified with BAE-1 (Figure 4a).



Figure 4. (a) Stress relaxation of elastomeric dynamic networks based on Jeffamine D2000 BAE-1 (red) and BAE-1-OH (black) at 180 °C. (b) Respective Arrhenius plot derived activation energy of flow, obtained from measurements at 180–150 °C. (c) Creep recovery experiments performed at 80 °C with a remaining permanent deformation of 0.02%.

This is in line with reported studies, which showed that a synergetic effect is typically observed when multiple dynamic chemistries are implemented in a material.^{20,50} Besides, when stress relaxation experiments were performed at different temperatures for the obtained materials, a high temperature dependence was observed, resulting in a flow activation energy $(E_{a(flow)})$ of 110-240 kJ mol⁻¹ (Table 1). Such high temperature dependent dynamic behavior favors the creation

of dynamic, yet creep resistant elastomers,⁴³ as very recently reported with addition-type reprocessable elastomers.⁶⁴

Hence, because of the high activation energy derived from the respective Arrhenius plots (i.e., 163 ± 12 kJ mol⁻¹ and 242 \pm 8 kJ mol⁻¹ for BAE-1 and BAE-1-OH, respectively) (Figure 4b), both elastomers demonstrated strong creep resistance at elevated temperatures (50 and 80 °C). Indeed, upon exposure to 2 kPa shear stress for 20 min, the materials displayed merely ~0.01% (50 °C) and ~0.02% (80 °C) remaining strain as permanent deformation after a recovery period of 20 min (Figure 4c and Figure S16).

CANs Combining β -Amino and β -Hydroxyl Groups. To take this approach a step further, the effect of a potential double neighboring group participation (NGP) on the exchange rate was investigated. Indeed, in addition to the β amino group, which is hypothesized to be responsible for creating an activation of the ester bond via coordination of the alcohol proton and the ester-carbonyl group, a β -hydroxyl group can be simultaneously introduced. Such a β -hydroxyalkyl ester, was in fact already reported by Leibler and co-workers⁶ in the seminal paper of vitrimers.

Herein, this NGP effect was introduced using a β -hydroxyalkyl functional bis-acrylate moiety (Figure 5a). While the β -amino moiety activates the electrophile side of the ester group, the β -hydroxyalkyl one allows for swift reactivity on the nucleophile side. For the corresponding CANs, further referred to as BPAE materials, bisphenol A glycerolate diacrylate (BPADA) was used in combination with similar amines as for the β -amino ester networks described above (Table 2). The synthesized densely cross-linked polymer networks displayed a T_g of -40 °C (BPAE-1), 30 °C (BPAE-2) and 70 °C (BPAE-3), leading to elastomeric as well as rigid polymer samples while being thermally stable beyond 300 °C (Table 2, Figures S17–S21).

More specifically, the network composition BPAE-3 (Figure 5a) resulted in a network with a T_g of 70 °C, a degradation onset temperature of 310 °C with less than 1% weight loss over 2 h at 160 °C and less than 2% weight loss over 1 h at 200 °C (Figure S22). Moreover, despite having activated ester bonds, BPAE-3 was demonstrated to be hydrolytically resistant when immersed in demineralized water up to 10 days at room temperature. This network showed a soluble fraction of less than 1% while the swelling degree increases with time from 7.2%, 11.2% and 18.1%, after 1, 4, and 10 days, respectively. Yet, when the network BPAE-3 was subjected to boiling water for 24 h, the network hydrolyzed resulting in a soft and sticky residue and a turbid dispersion. This indicates the opportunity to apply optimized hydrolytic conditions in order to recover, for example, fibers in composite applications.

Because of the accelerated dynamic covalent exchange as a result of an increased number of hydroxyl moieties, decreased cross-linking density, and a double NGP, reprocessing of the network BPAE-3 was conducted at shorter times and lower temperatures compared to the CANs described earlier, i.e., within 30 min at 150 °C with a pressure of 4 tons (Figure 5b).

When assessing the rheological behavior, stress relaxation measurements demonstrate that the thermally activated network rearrangement allowed for relaxation of the applied stress in the investigated temperature range from 140 to 180 °C (Figure 5c), with a resulting temperature dependent viscous flow represented by a flow activation energy of 156 ± 8 kJ mol⁻¹ (Figure 5d). This is similarly high as for the above-discussed β -amino ester networks and is again ascribed to

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Figure 5. (a) CAN obtained via aza-Michael addition of MBCA to BPADA (BPAE-3), with the potential of two neighboring group effects originating from a β -amino (green) and a β -hydroxyl moiety (blue). (b) Picture of compression molding of BPAE-3. (c) Normalized stress relaxation measurements. (d) Corresponding Arrhenius plot as a function of 1000/*T*. (e) Frequency sweep measurement showing a decreased elastic plateau modulus with increased temperature. (f) Scheme for the dissociative and associative dynamic covalent bond exchange.

	Table 2. Overview of Com-	positions and Physical P	Properties of β -Aming	Ester-Based CANs Showing	z a Double NGP Effect
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CAN	acrylate	amine	T_{gDSC}^{a} (°C)	$T_{d-95\%}^{b}$ (°C)	soluble fraction ^{c} (%)	swelling degree ^d (%)	$E_{\rm a(flow)}~(\rm kJ~mol^{-1})$	G'^e (MPa)
BPAE-1	BPADA	Jeffamine	-40	340	14	425	180 ± 24	0.27 ± 0.003
BPAE-2	BPADA	Priamine	30	340	2.8	95	121 ± 7	0.62 ± 0.03
BPAE-3	BPADA	MBCA	70	310	5.0	90	156 ± 8	0.62 ± 0.01
^a T obtained	d from DS(C-analysis ^b T	'GA onset-tem	peratures after	5% weight-loss ^c obta	ined after Soxhlet-extr	action for 24 h in T	THE ^d obtained

 T_{g} obtained from DSC-analysis, TGA onset-temperatures after S% weight-loss, "obtained after Soxhlet-extraction for 24 h in THF, "obtained after swelling in THF for 7 days at rt. ^e obtained from a time sweep measurement at 120 °C.

originate from a combination of transesterification and dynamic aza-Michael reaction, albeit the transesterification reaction is likely to be dominant in the probed temperature window. A frequency sweep of the glassy polymer network (BPAE-3), in combination with the non-normalized relaxation modulus (G(t)) obtained from stress relaxation measurements, revealed the coexistence of transesterification while also showing partial de-cross-linking. Indeed, the frequency sweep showed a decrease of the material's shear storage modulus (G') upon increasing the temperature while a shift of the anticipated

crossover was apparent (Figure 5e). This is in accordance with the observed G(t) that also decreased with increased temperature (Figures S23 and S24), which is indicative for a decrease of cross-linking density in dissociative covalent dynamic polymer networks,⁶⁵ in this particular case related to the dynamic aza-Michael reaction (Figure 5f).

The coexistence of both dynamic aza-Michael and transesterification to dissipate applied stress in a material also resulted in a high flow activation energy for BPAE-1 and BPAE-2 (Figure S25) and demonstrates the broad applicability

into different matrices. In combination with the results obtained from the kinetic study (Figure 1), it was concluded that transesterification was likely to occur at temperatures below 120 °C, whereas the dynamic aza-Michael reaction is negligible under these conditions. This is supported by the high creep-resistance at 80 °C for elastomeric network BPAE-1 (Figure S26). Yet, at elevated temperatures the dynamic aza-Michael reaction mechanism contributed to the overall dynamic covalent exchange related network mobility. Accordingly, in a frequency sweep of BPAE-1 upon heating, the elastic plateau modulus remains almost unaltered up to 120 °C, whereas a continuous drop in G' was detected beyond 140 °C (Figure S27).

Reprocessability. Next, network BPAE-3 was reprocessed up to 10 times with similar conditions (30 min compression at 150 °C with a pressure of 4 tons), further referred to as R_0 up to R₁₀. The network kept its ability for compression molding, showing each time homogeneous, transparent samples, even after up to 10 additional reprocessing steps using the aforementioned processing conditions (Figure 6a, Figure \$28). Subsequently, soluble fraction experiments of a piece of the material resulted in soluble fractions of 5.0%, 15.2%, and 11.9% for $R_{0^{\prime}}$ $R_{4^{\prime}}$ and R_{10} while the swelling degree accounted to 88%, 97%, and 108%, respectively. The increase in soluble fraction and swelling ratio is attributed to the partially dissociative nature of the exchange reactions. Reprocessability of the samples was confirmed on behalf of BPAE-3 by examining their stress relaxation properties (Figure S29), represented by their Arrhenius plots (Figure 6b) as well as frequency sweep experiments (Figure 6c, Figures S30 and S31). In addition, the recorded FTIR spectra and thermal analyses supported the conclusion that the chemical composition and material properties were maintained after 10 recycling cycles (Figure S32).

In the reprocessed sample R₁₀, a small decrease in the storage modulus G' of the elastic plateau modulus at 180 $^{\circ}$ C was observed (Figure 6c), which can again be linked to the dissociative nature of the retro aza-Michael reaction and partial reformation of the network upon reprocessing. Indeed, upon partial dissociation and re-formation of acrylate moieties, partial homopolymerization/transfer reaction or amidation via the re-formed secondary amines, particularly at elevated temperatures, might occur. The homopolymerization of acrylate groups was experimentally also observed in the model study (Figure S5), and when five subsequent cycles of stress relaxation measurements were performed at 150 and 180 °C (Figure S33), a slight increase in relaxation modulus and the respective relaxation time was apparent at 180 °C as a result of minor side reactions. Nonetheless, reprocessability tests showed that these reactions barely affected the overall reprocessing properties of the herein presented networks.

CONCLUSION

In this study, β -amino esters were demonstrated to inherently behave as dynamic moieties in CANs, with a combination of dissociative and associative dynamic behavior that is easily accessible by simply combining acrylic and amino functionalities. This concept was first demonstrated on model compounds and then in bulk materials solely relying on dynamic (retro) aza-Michael reaction as well as for transesterification in combination with pendent hydroxyl moieties. Catalyst-free reprocessing of polyester networks was achieved with β hydroxyl groups at 150 °C within 30 min. This was



Figure 6. (a) Reprocessing of β -amino ester network BPAE-3 up to 10 times. (b) Arrhenius plot derived from the stress relaxation experiments performed after the initial processing (R₀ (red)) as well as 4 and 10 times reprocessing (R₄ (blue) and R₁₀ (green), respectively). (c) Corresponding frequency sweep at 180 °C.

shown for highly cross-linked materials with varying $T_{\rm g}$ ranging from elastomeric (-60 °C) to glassy materials (90 °C). The reprocessing ability of the materials was demonstrated for up to 10 cycles.

This approach allows for polymer material design of tailored viscosity profiles. On the one hand, network connectivity is reduced with the dissociative part, while on the other hand, a certain degree of connectivity is maintained with the support of the associative mechanism. Yet the thermally reversible bonds are positioned on different sides of the electrophilic center of the ester group, using different reaction mechanisms, acting synergetic and rather orthogonally. In view of the simplicity of the herein presented approach, the large amount of available building blocks, and the fact that β -amino esters possess inherently thermally activated dynamic bonds, these kinds of CANs are expected to contribute significantly to the current processing and recycling limitations of thermosets. Further-

more, the robustness and versatility of this system were demonstrated by combining multifunctional acrylates with amino groups on primary and secondary carbons of small or macromolecular entities. It is therefore expected to be rapidly picked up by interdisciplinary working scientists in many application areas ranging from (photocurable) coatings and adhesives to bulk materials. Because poly(β -amino ester) materials were explored with regard to their degradability, ⁵⁵ β -amino esters might also be of importance in the end-of-life recyclability and degradability of plastic materials. Lastly, this readily accessible chemistry, bridging from organic chemistry to polymer materials, can be used for drop-in technologies in bulk (bio)materials.

EXPERIMENTAL SECTION

Material. Acetonitrile (99.9%, HPLC gradient grade), benzyl alcohol (\geq 99%), benzyl acrylate (\geq 99%, contains hydroquinone monomethyl ether (MEHQ) as inhibitor), bisphenol A glycerolate (1 glycerol/phenol) diacrylate (contains 250-500 ppm MEHQ as inhibitor), *n*-butylamine (\geq 99%), dibutylamine (\geq 99%), *N*,*N*diisopropylethylamine (DIPEA, ≥99%) 2-ethylhexyl acrylate (98%, contains MEHQ as inhibitor), 2-ethylhexylamine (98%), Nmethylbutylamine (≥98%), pentaerythritol triacrylate (PTA, technical grade, contains 600 ppm of MEHQ as inhibitor), trimethylolpropane triacrylate (TMPTA, technical grade, contains 300-400 ppm of MEHQ as inhibitor), n-octylamine (99%) were purchased from Sigma-Aldrich. Tetrahydrofuran (THF) and *n*-hexane were purchased from Acros Organics. 4,4'-Methylenebis(cyclohexylamine) (MBCA, >98%) was purchased from TCI. Jeffamine D2000 was kindly provided by Huntsman, and Priamine 1074 was 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).

Liquid chromatography–mass spectrometry (LCMS) combined with electrospray ionization mass spectrometry (ESI-MS) was measured with an Agilent technologies 1100 series LC/MSD system equipped with a diode array detector and a single quad MS detector (Agilent G1956B) with an electrospray source for classic reversed phase LCMS and MS analysis. Analytic reversed phase high-performance liquid chromatography (HPLC) was performed with a Phenomenex Kinetex C18 column (5 μ m, 150 mm × 4.6 mm) using a solvent gradient (0–100% acetonitrile in H₂O in 6 min). The eluting compounds (15 μ L injected from 1 mg·mL⁻¹ in acetonitrile) were detected via UV detection (λ = 214 nm), and ESI-MS results were recorded in positive mode.

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·min⁻¹ from 25 to 800 °C for the dynamic mode. Isothermal measurements were conducted under nitrogen atmosphere at 160 °C for 120 min and 200 °C for 60 min.

Differential scanning calorimetry (DSC) analyses were performed with a Mettler Toledo instrument 1/700 under nitrogen atmosphere at a heating rate of 10 K·min⁻¹ either from -100 to 100 °C for elastic materials or from 0 to 150 °C for glassy materials.

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·s⁻¹, and a strain of 0.1% (for materials containing tris-functional acrylates) and 1% (for materials containing bis-functional acrylates, or elastic materials) was applied. For all rheology experiments, the

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applied stress comprised the linear viscoelastic region at the measured temperatures. For amplitude sweep experiments, the strain was varied from 0.01% to 100% with an oscillating frequency of 5 rad s^{-1} . For time sweep experiments a strain of 0.1% or 1% was applied with a frequency of 5 rad \cdot s⁻¹ for a duration of 300 s at 120 °C and G' and G'' were followed over time. The reported G' values were averaged and taken from the second measurement after an initial 5 min time sweep to remove a possible thermal history. For stress relaxation experiments, a strain of 0.1%, or 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. For frequency sweep measurements, a strain of 1% with a normal force of 0.2 N (BPAE-1) and 1 N (BPAE-3) was applied and a frequency range from 100 to 0.1 rad s^{-1} was screened by following the evolution of G' and G" at a constant temperature. Creep recovery experiments were performed by applying no strain for a duration of 300 s, which was followed by applying 2 kPa shear stress for 1200 s and a recovery period of 1200 s at 80 and 50 °C. Creep recovery measurements were preceded by a measurement at 80 $^\circ C$ to remove a possible thermal history.

Reprocessability. To reprocess the network, the polymer was broken into pieces and placed into a rectangular mold (A, 70 mm \times 40 mm \times 2 mm; B, 30 mm \times 15 mm \times 2 mm) for compression molding. This assembly was placed in a 150-180 °C preheated compression press for 1 min under 0.5 metric tons of pressure. Then the pressure was increased to 3 or 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. The temperature and pressing time were adjusted according to the material based on its T_{α} and cross-linking density. Hence, highly cross-linked materials obtained using tris-functional acrylates were pressed at 180 °C for 60 min depending on their relaxation behavior, whereas bis-acrylate based materials were pressed at 150 °C for 30 min. For instance, pentaerythritol triacrylate and trimethylolpropane triacrylate based networks were processed at 180 °C for 60 min applying 3 tons (Jeffamine) or 60 min with 4 tons (4,4'methylenebis(cyclohexylamine)), whereas bisphenol A glycerolate diacrylate was pressed at 150 °C for 30 min applying 4 tons.

Solubility tests were performed via Soxhlet extraction in refluxing THF for 24 h with a sample weight of around 100-200 mg. Then, the solvent was removed, and the sample was dried under vacuum for 2 days at 100 °C. The soluble fraction was calculated using eq 1. Swelling tests were performed by immersing a sample of 40-60 mg in 3 mL of THF at room temperature for 7 days, and the swelling ratio was calculated using eq 2. Hydrolysis tests were performed by immersing around 90 mg of BPAE-3 in 3 mL of demineralized water for 1, 4, and 10 days, drying the samples in a vacuum oven at 120 °C and determining the respective soluble fraction and swelling ratio according to eqs 1 and 2. A hydrolysis test at elevated temperatures was performed by placing a piece of BPAE-3 (110 mg) in a glass vial with 5 mL of H₂O, which was closed with a septum under nitrogen atmosphere. The material was monitored in water for 24 h at room temperature and remained visibly intact. Thereafter, the vial was placed in a heated oil bath (110 °C) for a hot water hydrolysis test.

soluble fraction (%) = 100 ×
$$\frac{(m_{\rm i} - m_{\rm d})}{m_{\rm i}}$$
 (1)

swelling ratio (%) =
$$100 \times \frac{(m_{\rm s} - m_{\rm i})}{m_{\rm i}}$$
 (2)

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

Synthetic Procedures. 2-Ethylhexyl 3-(Butyl(methyl)amino)propanoate (1). N-Methylbutylamine (8.53 g, 0.0979 mol, 1.2 equiv) was combined with 2-ethylhexyl prop-2-enoate (15.19 g, 0.0824 mol, 1 equiv) and stirred at 70 °C for 72 h. The product was then taken up in 30 mL of *n*-hexane (30 mL), washed with water (3×20 mL), once with brine (1×20 mL), and dried over Mg(SO₄), after which *n*hexane was removed and the pale yellow oil was dried in a vacuum

oven overnight at 40 °C. Yield = 95% (21.26 g, 0.0783 mol). $^1\mathrm{H}$ NMR (300 MHz, CDCl₃, δ ppm): 0.82–0.95 m((-CH₂-CH₃)₃), 1.12-1.49 $m((-CH_2-CH_2-CH_2-CH_3) (-CH-CH_2-CH_3)$ $(-CH_2-CH_2-CH_2(CH_3)), 1.49-1.64 m(CH_2-CH(CH_2)-CH_2),$ 2.22 s(N-CH₃), 2.30-2.37 m(-CH₂-CH₂-N-), 2.43-2.50 and 2.65-2.73 m(-N(CH₃)-CH₂-CH₂-(C=O)-O-) and 3.99 (dd, J = 5.8, 0.9 Hz; $(-(C=O)-O-CH_2-CH(CH_2)-CH_2-)$. ¹³C NMR (300 MHz, CDCl₃, δ ppm) 172.91 (CH₂-(C=O)-O-CH₂), 66.82 (-(C=O)-O-CH₂-CH₂), 57.23 (-CH₂-CH₂-N-), 52.89 (-N-CH₂-CH₂-), 41.94 (-N-CH₃), 38.73 (CH₂-CH-(CH₂)-CH₂), 32.62 (CH₂-CH₂-(C=O)), 30.40 (CH-CH₂-CH₂), 29.44 (CH2-CH2-CH2-N), 28.91 (CH-CH2-CH2-CH2-CH2-), 23.77 and 22.95 (CH₂-CH₂-CH₃, CH-CH₂-CH₃), 20.60 (CH₃-CH₂- $(CH_2)_2 - N)$, 14.01 $(CH - (CH_2)_3 - CH_3, CH_3 - (CH_2)_3 - N)$, 10.97 $(CH - CH_2 - CH_3)$. ESI-MS m/z: $[M + H]^+$ for $C_{16}H_{34}NO_2^+$; calculated 272.258; found 272.300. IR (ATR platinum diamond), v $[cm^{-1}]$: 2956 (C-CH₃), 2929 (CH₂), 2860 (C-CH₃), 2788 (N-CH₃), 1735 (C=O), 1461 (CH₂), 1379 (CH₃), 1176 and 1035 (C- $O-C_{ester}$).

Kinetic Model Study. For kinetic experiments monitoring the transesterification 1 equiv of model compound (1) (400 mg) was mixed with 12.5 equiv of benzyl alcohol (2 g) in a sealable glass vial, bubbled with nitrogen at room temperature and kept under nitrogen atmosphere. The vial was placed in a heated oil bath with the mixture being stirred. The kinetic experiments were performed at 80, 100, 110, 120, and 140 °C for up to 3 days during which samples were collected from this mixture, dissolved in CDCl₃, and the reaction was followed via ¹H NMR by assessing the disappearance of the signal at 3.91 ppm belonging to 1 which was referenced against the appearance of the signal at 3.42 ppm related to 2-ethylhexyl alcohol. Kinetic experiments using additional tertiary amine (DIPEA) or secondary amine (dibutyl amine) as "external" catalyst 5 mol % of the respective compound compared to 1 were added, and the exchange reaction was monitored at 120 °C for 2 days. For kinetic experiments monitoring the dynamic aza-Michael reaction 1 equiv of model compound (1)(400 mg) was mixed with 6 equiv of benzyl acrylate (1.43 g) in a sealable glass vial, bubbled with nitrogen at room temperature, and kept under nitrogen atmosphere. The vial was placed in a heated oil bath with the mixture being stirred. The kinetic experiments were performed at 100, 130, 140, 150, and 160 °C for up to 2 days during which samples were collected from this mixture, dissolved in CDCl₃, and the reaction was followed via ¹H NMR by assessing the disappearance of the signal at 4.02 ppm belonging to 1 which was referenced against the appearance of the signal at 4.10 ppm related to 2-ethylhexyl acrylate. Following the assumption of a stationary state, consequently mimicking a first order reaction, the kinetic reaction constants (k) were derived from the slope of the linear decay of the first few points of time. The logarithmic reaction constants $(\ln(k))$ were then plotted against $1000T^{-1}$ in an Arrhenius plot to compare the relative temperature dependent behavior. An activation energy was calculated from the obtained slope by eq 3.22

$$\ln(k) = -\frac{E_a}{RT} \tag{3}$$

Network Synthesis. For the herein investigated materials the multifunctional acrylate and the multifunctional primary amino compounds were weighed with a ratio of acrylate to primary amine moieties of 1:0.5 and 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) targeting 3-10 g of the resulting material. When 4,4'-methylenebis(cyclohexylamine) was used, the sample was allowed to warm up to 70 °C in an oven in order to melt the amine. Similarly, when bisphenol A glycerolate diacrylate was used, the sample was warmed up in an oven at 70 °C to lower the viscosity of the acrylate for facilitated mixing. Then, the plastic cup was placed in an oven at 70–80 °C for 48–72 h to complete the 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 procedures.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c03316.

NMR spectra, LCMS-ESI-MS measurements, IR spectra, kinetics plots, DSC and TGA thermograms, stress relaxation data, frequency sweeps, and images of reprocessed materials (PDF)

AUTHOR INFORMATION

Corresponding Author

Filip E. Du Prez – Polymer Chemistry Research Group, Center of Macromolecular Chemistry (CMaC), Department of Organic and Macromolecular Chemistry, Faculty of Science, Ghent University, Ghent B-9000, Belgium; orcid.org/ 0000-0001-7727-4155; Email: filip.duprez@ugent.be

Authors

- Christian Taplan Polymer Chemistry Research Group, Center of Macromolecular Chemistry (CMaC), Department of Organic and Macromolecular Chemistry, Faculty of Science, Ghent University, Ghent B-9000, Belgium;
 orcid.org/0000-0002-8078-0953
- Marc Guerre Polymer Chemistry Research Group, Center of Macromolecular Chemistry (CMaC), Department of Organic and Macromolecular Chemistry, Faculty of Science, Ghent University, Ghent B-9000, Belgium; Laboratoire des IMRCP, Université de Toulouse, CNRS UMRS623, Université Paul Sabatier, 31062 Toulouse, France; Orcid.org/0000-0003-1410-9923

Complete contact information is available at: https://pubs.acs.org/10.1021/jacs.1c03316

Author Contributions

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

BAE-#, β-amino ester network; BPAE-#, bisphenol A β-amino ester network; CAN, covalent adaptable network; CDCl₃, deuterated chloroform; DIPEA, *N*,*N*-diisopropylethylamine; DSC, differential scanning calorimetry; $E_{a(flow)}$, activation energy of flow; ESI-MS, electrospray ionization mass spectrometry; FTIR, Fourier transform infrared spectroscopy; LCMS, liquid chromatography–mass spectrometry; NGP, neighboring group participation; NMR, nuclear magnetic resonance; PTA, pentaerythritol triacrylate; TGA, thermogravimetric analysis; T_{gy} glass transition temperature; THF, tetrahydrofuran; TMPTA, trimethylolpropane triacrylate

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REFERENCES

(1) Horejs, C. Solutions to plastic pollution. *Nat. Rev. Mat* 2020, 5 (9), 641–641.

(2) Billiet, S.; Trenor, S. R. 100th Anniversary of Macromolecular Science Viewpoint: Needs for Plastics Packaging Circularity. *ACS Macro Lett.* **2020**, *9* (9), 1376–1390.

(3) 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.

(4) 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.

(5) Scott, T. F.; Schneider, A. D.; Cook, W. D.; Bowman, C. N. Photoinduced Plasticity in Cross-Linked Polymers. *Science* **2005**, *308* (5728), 1615–1617.

(6) Montarnal, D.; Capelot, M.; Tournilhac, F.; Leibler, L. Silica-like malleable materials from permanent organic networks. *Science* **2011**, 334 (6058), 965–968.

(7) 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.

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

(9) 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.

(10) Osthoff, R. C.; Bueche, A. M.; Grubb, W. T. Chemical Stress-Relaxation of Polydimethylsiloxane Elastomers1. *J. Am. Chem. Soc.* **1954**, 76 (18), 4659–4663.

(11) 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.

(12) Bowman, C. N.; Kloxin, C. J. Covalent adaptable networks: reversible bond structures incorporated in polymer networks. *Angew. Chem., Int. Ed.* **2012**, *51* (18), 4272–4274.

(13) 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* (1), 175–198.

(14) 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 Sustainable Chem. Eng.* **2018**, *6* (9), 11145–11159.

(15) Terryn, S.; Brancart, J.; Lefeber, D.; Van Assche, G.; Vanderborght, B. Self-healing soft pneumatic robots. *Sci. Robot* **2017**, *2* (9), eaan4268.

(16) Chapelle, C.; Quienne, B.; Bonneaud, C.; David, G.; Caillol, S. Diels-Alder-Chitosan based dissociative covalent adaptable networks. *Carbohydr. Polym.* **2021**, *253*, 117222.

(17) Rekondo, A.; Martin, R.; Ruiz de Luzuriaga, A.; Cabañero, G.; Grande, H. J.; Odriozola, I. Catalyst-free room-temperature selfhealing elastomers based on aromatic disulfide metathesis. *Mater. Horiz.* **2014**, *1* (2), 237–240.

(18) 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. Horiz.* **2016**, *3* (3), 241–247.

(19) 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.

(20) 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.

(21) 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.

(22) 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.

(23) 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.

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

(25) 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.

(26) Capelot, M.; Montarnal, D.; Tournilhac, F.; Leibler, L. Metalcatalyzed transesterification for healing and assembling of thermosets. *J. Am. Chem. Soc.* **2012**, *134* (18), 7664–7667.

(27) Wang, C.; Goldman, T. M.; Worrell, B. T.; McBride, M. K.; Alim, M. D.; Bowman, C. N. Recyclable and repolymerizable thiol–X photopolymers. *Mater. Horiz.* **2018**, *5* (6), 1042–1046.

(28) Guerre, M.; Taplan, C.; Nicolay, R.; Winne, J. M.; Du Prez, F. E. Fluorinated Vitrimer Elastomers with a Dual Temperature Response. J. Am. Chem. Soc. 2018, 140 (41), 13272–13284.

(29) 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.

(30) Taplan, C.; Guerre, M.; Winne, J. M.; Du Prez, F. E. Fast processing of highly crosslinked, low-viscosity vitrimers. *Mater. Horiz.* **2020**, 7 (1), 104–110.

(31) Taynton, P.; Ni, H.; Zhu, C.; Yu, K.; Loob, S.; Jin, Y.; Qi, H. J.; Zhang, W. Repairable Woven Carbon Fiber Composites with Full Recyclability Enabled by Malleable Polyimine Networks. *Adv. Mater.* **2016**, 28 (15), 2904–2909.

(32) Whiteley, J. M.; Taynton, P.; Zhang, W.; Lee, S. H. Ultra-thin Solid-State Li-Ion Electrolyte Membrane Facilitated by a Self-Healing Polymer Matrix. *Adv. Mater.* **2015**, *27* (43), 6922–6927.

(33) 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.

(34) Jin, K.; Li, L.; Torkelson, J. M. Recyclable Crosslinked Polymer Networks via One-Step Controlled Radical Polymerization. *Adv. Mater.* **2016**, *28* (31), 6746–6750.

(35) 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.

(36) Snyder, R. L.; Fortman, D. J.; De Hoe, G. X.; Hillmyer, M. A.; Dichtel, W. R. Reprocessable Acid-Degradable Polycarbonate Vitrimers. *Macromolecules* **2018**, *51* (2), 389–397.

(37) 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.

(38) Rottger, M.; Domenech, T.; van der Weegen, R.; Breuillac, A.; Nicolay, R.; Leibler, L. High-performance vitrimers from commodity thermoplastics through dioxaborolane metathesis. *Science* **2017**, *356* (6333), 62–65.

(39) Zhang, B.; Digby, Z. A.; Flum, J. A.; Chakma, P.; Saul, J. M.; Sparks, J. L.; Konkolewicz, D. Dynamic Thiol–Michael Chemistry for Thermoresponsive Rehealable and Malleable Networks. *Macromolecules* **2016**, *49* (18), 6871–6878.

(40) 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.

(41) Van Zee, N. J.; Nicolaÿ, R. Vitrimers: Permanently crosslinked polymers with dynamic network topology. *Prog. Polym. Sci.* **2020**, *104*, 101233.

(42) Podgorski, 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 Continu-

pubs.acs.org/JACS

ous Development and Improvements in Covalent Adaptable Networks (CANs). Adv. Mater. 2020, 32 (20), 1906876.

(43) Guerre, M.; Taplan, C.; Winne, J. M.; Du Prez, F. E. Vitrimers: directing chemical reactivity to control material properties. *Chem. Sci.* **2020**, *11* (19), 4855–4870.

(44) 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.

(45) 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.

(46) 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.

(47) Zhang, H.; Majumdar, S.; van Benthem, R. A. T. M.; Sijbesma, R. P.; Heuts, J. P. A. Intramolecularly Catalyzed Dynamic Polyester Networks Using Neighboring Carboxylic and Sulfonic Acid Groups. *ACS Macro Lett.* **2020**, *9* (2), 272–277.

(48) Delahaye, M.; Tanini, F.; Holloway, J. O.; Winne, J. M.; Du Prez, F. E. Double neighbouring group participation for ultrafast exchange in phthalate monoester networks. *Polym. Chem.* **2020**, *11* (32), 5207–5215.

(49) Podgorski, M.; Mavila, S.; Huang, S.; Spurgin, N.; Sinha, J.; Bowman, C. N. Thiol-Anhydride Dynamic Reversible Networks. *Angew. Chem., Int. Ed.* **2020**, *59* (24), 9345–9349.

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

(51) 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.

(52) Podgórski, M.; Spurgin, N.; Mavila, S.; Bowman, C. N. Mixed mechanisms of bond exchange in covalent adaptable networks: monitoring the contribution of reversible exchange and reversible addition in thiol–succinic anhydride dynamic networks. *Polym. Chem.* **2020**, *11* (33), 5365–5376.

(53) 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. Chem., Int. Ed.* **2020**, *59* (9), 3609–3617.

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

(55) Anderson, D. G.; Tweedie, C. A.; Hossain, N.; Navarro, S. M.; Brey, D. M.; Van Vliet, K. J.; Langer, R.; Burdick, J. A. A Combinatorial Library of Photocrosslinkable and Degradable Materials. *Adv. Mater.* **2006**, *18* (19), 2614–2618.

(56) Lynn, D. M.; Langer, R. Degradable Poly(β -amino esters): Synthesis, Characterization, and Self-Assembly with Plasmid DNA. J. Am. Chem. Soc. **2000**, 122 (44), 10761–10768.

(57) Genest, A.; Portinha, D.; Fleury, E.; Ganachaud, F. The aza-Michael reaction as an alternative strategy to generate advanced silicon-based (macro)molecules and materials. *Prog. Polym. Sci.* 2017, 72, 61–110.

(58) 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.

(59) Zhang, H.; Bre, 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.

(60) Baruah, R.; Kumar, A.; Ujjwal, R. R.; Kedia, S.; Ranjan, A.; Ojha, U. Recyclable Thermosets Based on Dynamic Amidation and Aza-Michael Addition Chemistry. *Macromolecules* **2016**, 49 (20), 7814–7824.

(61) Stukenbroeker, T.; Wang, W.; Winne, J. M.; Du Prez, F. E.; Nicolaÿ, R.; Leibler, L. Polydimethylsiloxane quenchable vitrimers. *Polym. Chem.* **201**7, *8* (43), 6590–6593.

(62) Altuna, F. I.; Hoppe, C. E.; Williams, R. J. J. Epoxy vitrimers with a covalently bonded tertiary amine as catalyst of the transesterification reaction. *Eur. Polym. J.* **2019**, *113*, 297–304.

(63) 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.

(64) Li, L.; Chen, X.; Jin, K.; Rusayyis, M. B.; Torkelson, J. M. Arresting Elevated-Temperature Creep and Achieving Full Cross-Link Density Recovery in Reprocessable Polymer Networks and Network Composites via Nitroxide-Mediated Dynamic Chemistry. *Macromolecules* **2021**, *54* (3), 1452–1464.

(65) 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.