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Exploring Transamidation and Chemical Recycling of β-Amino Amide-Derived Covalent Adaptable Networks

Loc Tan Nguyen [a], Adithya Tharayil [a], Nezha Badi [a], Johan M. Winne [b]*, Filip E. Du Prez [a]*

[a] Polymer Chemistry Research Group, Centre of Macromolecular Chemistry (CMaC), Department of Organic and Macromolecular Chemistry, Faculty of Sciences, Ghent University, Krijgslaan 281 S4, 9000 Ghent, Belgium.

[b] Laboratory of Organic Synthesis, Department of Organic and Macromolecular Chemistry, Faculty of Sciences, Ghent University, Krijgslaan 281 S4, 9000 Ghent, Belgium.

* E-mail: Filip.DuPrez@UGent.be and Johan.Winne@UGent.be

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Abstract

The growing environmental challenge of non-recyclable thermosets underscores the urgent need for sustainable alternatives. Covalent adaptable networks (CANs) containing dynamic β-amino amide moieties have emerged as promising reprocessable polymer networks, combining mechanical robustness with recyclability. In this work, we elucidate the exchange kinetics of both the well-established (retro) aza-Michael addition and a newly identified transamidation pathway that is operative in β-amino amides. Systematic catalyst screening reveals that acidic catalysts significantly enhance viscoelastic control, thereby improving (re)processing efficiency. Furthermore, we introduce a chemical recycling protocol that enables the recovery of the original amino building blocks with up to 86 % purity, demonstrating their direct use as feedstock in material (re)synthesis. These insights advance the fundamental understanding of dynamic bond

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exchange in β-amino amide based CANs and establish a viable route towards circular thermoset materials for numerous applications.

Introduction

Since their first introduction in the early 20th century, synthetic thermosets have undergone a remarkable development, playing a pivotal role in modern industry nowadays.[1] Their cross-linked polymeric structures impart a unique combination of low weight and high mechanical strength, making them indispensable in demanding applications ranging from aviation components to wind turbine blades.[2] However, the permanent network structure also renders thermosets intrinsically non-reprocessable, consequently consigning them to permanent waste at their end-of-life. This fact results in widespread challenges from both environmental and regulatory perspectives.[3,4]

Covalent adaptable networks (CANs), also referred to as dynamic covalent polymer networks, have emerged in recent decades as a promising approach to reconcile the durability of thermosets with reprocessability.[5–7] By incorporating exchangeable (or dynamic) linkages, CANs facilitate reprocessability of thermosets under specific stimuli such as heat or light, while (ideally) retaining the superior properties of polymeric networks.[6,8] A wide range of dynamic chemistry platforms have been introduced in CANs, including transesterifications,[9,10] vinylogous urethanes,[11,12] Diels–Alder,[13,14] dithioacetal,[15] and imine exchange,[16,17] a few of which have progressed toward commercial products.[18,19] Despite this progress, their practical adoption is still constrained due to their dynamicity-performance trade-off.[20,21] While dynamic bonds endow CANs with recyclability, they are typically labile (low activation energies - E_a), which can lead to premature bond exchange (i.e., flow or creep) under service conditions.[22] As a consequence, this phenomenon leads to an undesirable loss in designated performance of CANs, thus often not making them suitable to replace conventional thermosets. Addressing this long-standing limitation requires the

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development of suitable dynamic covalent chemistry (DCC) and/or technologies that combine robustness with controlled exchange reactivity.

Polyamides, long recognized for their outstanding thermal and chemical stability, are particularly attractive for advancing CAN performance.[23] However, this inherent stability of amide bonds also implies their relative inertness towards exchange reactions, resulting in their limited exploration as DCC-platform in CANs to date. In 2021, one of the first amide-based DCCs for CAN was reported by us and others through a dicarboxamide-imide equilibrium, governed by the imide ring size as an entropic factor,[24,25] facilitating reprocessing of materials through dissociative transamidation at elevated temperatures (> 150 °C) with high E_a ranging from 120 to 200 kJ·mol^{-1}. In the meantime, this DCC has shown its industrial potential in providing both creep resistance and recyclability, applicable for a wide range of applications.[26] Subsequently, Xu et al. introduced dynamic maleic acid-tertiary amide linkages, where reversible amidation between maleic anhydrides and secondary amines enabled efficient monomer recovery (> 94% yield) and closed-loop chemical recycling of cross-linked polymeric materials.[27] Although both platforms demonstrate the feasibility of recycling polyamide networks, their reliance on specific monomers (e.g., glutarate ester or secondary amine building blocks) may restrict broader applicability.

Building on our earlier investigation of dynamic β-amino esters (BAEs),[28] we recently developed reversible β-amino amides (BAAs) as the next-generation platform for recyclable polyamide networks (**Figure 1A**).[29] BAA-based CANs (BAANs) and their epoxy-derived materials exhibit excellent creep resistance (up to 120 °C) and hydrolytic stability under both acidic and basic conditions, while maintaining reprocessability.[29,30] Our initial study showed that BAAs undergo reversible dissociation into acrylamides and amines above 140 °C. However, their exchange kinetics and the effect of catalysis have not been studied in detail so far. Notably, in the related

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BAE networks, neighboring amino groups act as internal catalysts that also promote transesterification in the presence of hydroxyl groups in addition to retro-Michael reactions,[28,31] raising the question whether an analogous transamidation process could occur in BAA-promoted DCC.

The current study started with an explicit study of the reversible Michael addition kinetics, further investigating the dynamic exchange, influence of catalysts, and the chemical recyclability of BAANs (**Figure 1B**). Initially, small-molecule model studies have been conducted to elucidate exchange pathways and their kinetics. Then, catalysts of different chemical nature - ranging from acidic to basic nature have been introduced into BAANs, followed by rheological analysis to assess their effect on the viscoelasticity behavior. Based on the newly acquired insights, we also investigated chemical degradation strategies to recover original amino building blocks from the BAANs as recycled feedstock resources. These studies provide mechanistic insights into BAA-based DCC, including the experimental verification of an unusual transamidation pathway, and further identify BAANs as high-performance polyamide networks with the potential for recycling and reprocessing.

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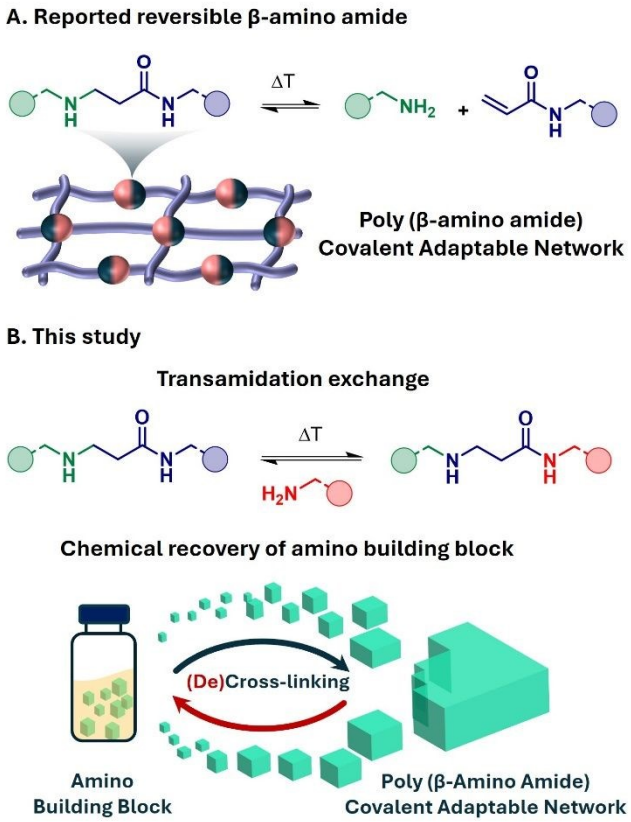

Figure 1. (A) Schematic representation of the previous study on materials including dynamic covalent β-amino amide chemistry.[29] **(B)** Representation of the present work: investigating transamidation, catalytic effects, and chemical recycling of CANs based on β-amino amide groups.

Results and discussion

Insights into dynamicity of the β-amino amide group

Although the dissociation of BAA was reported to occur at elevated temperatures beyond 140 °C,[29] we further investigate herein the exchange kinetics through small-molecule studies. For this purpose, N-benzyl-3-(methyl(octyl)amino)propenamide (**M**) was synthesized as the model BAA compound via the straightforward aza-Michael addition (details are given in **Section S3**, **Figure S1-S3)**. Firstly, the (retro) aza-Michael exchange was studied in a controlled exchange reaction between **M** and excess benzylamine (10 eq). As shown in **Figure 2A**, the exchange was monitored

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via proton nuclear magnetic resonance (^{1}H-NMR), by following the conversion over time of proton A (from **M** at 2.3 ppm) into proton R (at 2.9 ppm), which is attributed to (retro) aza-Michael exchange product **RA**. The formation of **RA** was further confirmed by electrospray ionization mass spectrometry (ESI-MS, **Figure S4**).

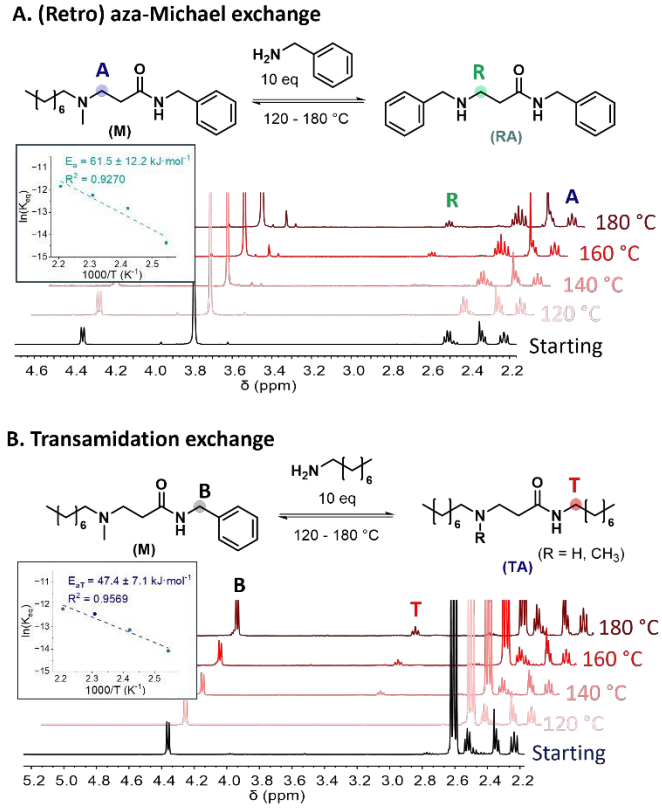

Figure 2. Reaction schemes and representative ^{1}H-NMR spectra with inset Arrhenius plots of the kinetic studies for: **(A)** reversible aza-Michael and **(B)** transamidation exchange of β-amino amide.

Kinetic studies were conducted at varying temperatures from 120 to 180 °C, enabling the determination of reaction constants at each temperature (**Figure S5**, **Table S1**). Based on these data, an Arrhenius plot was constructed, revealing an activation energy (E_a) of 61.5 kJ·mol^{-1}, consistent with reported values for (most of) reversible Michael adducts ranging from 50 to 80 kJ·mol^{-1}.[28,32,33]

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Subsequently, we uncovered an unsuspected transamidation pathway operating in these reactions by repeating the same exchange experiment with BAA **M** and an excess of octylamine (10 eq). Interestingly, alongside the expected (reversible) aza-Michael exchange product, analysis of the reaction mixture by ^{1}H-NMR spectroscopy also revealed new resonances that are characteristic of a transamidation reaction: benzylic proton B at 4.4 ppm (from **M**) is indeed being converted into methylene proton T (at 3.3 ppm) belonging to trans-amidated adduct **TA** (**Figure 2B**). The formation of TA was observed at temperatures above 140 °C, and thus showed similar kinetics compared to the (retro)-aza-Michael pathway. It is worth noting that the asymmetric structure of model compound M - with aliphatic and benzylic substituents - allowed for the exclusive monitoring of transamidation by ^{1}H-NMR, since the possible (retro) aza-Michael product (i.e., N-benzyl-3-(octylamino)propanamide) would exhibit identical proton resonances. The formation of the transamidation product **TA** was additionally confirmed by ESI-MS (**Figure S6**). From the integration in the NMR measurements, Arrhenius plots (**Figure S7** and **Table S2**) revealed an E_a of 47.4 kJ·mol^{-1}, which is a bit higher than the one reported for the transesterifications of BAE (35 kJ·mol^{-1}).[28]

Unlike transesterification, such direct transamidation is more challenging and typically requires catalysts, or high temperatures, and is thus unexpected in these systems.[34–38] Herein, we propose two possible reasonable mechanistic pathways, which are presented in **Figure 3** and are both related to a neighbouring group effect of the β-amine functionality.

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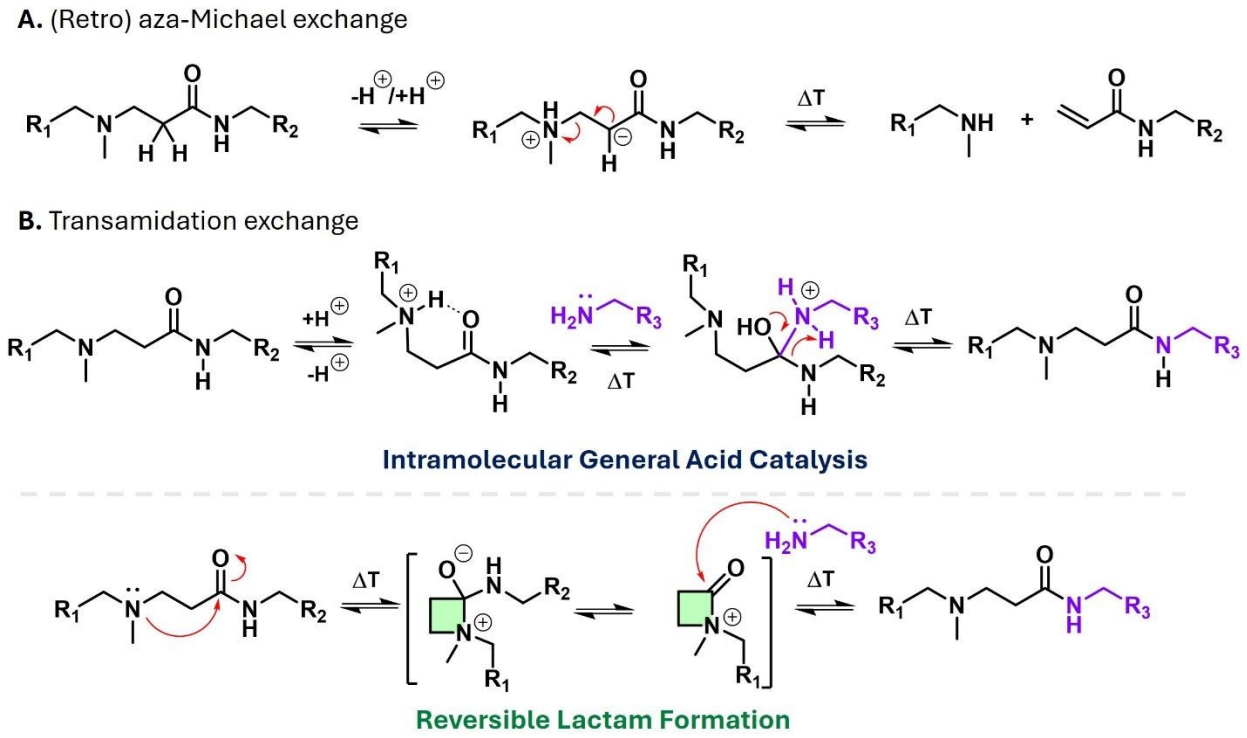

Figure 3. Proposed mechanism of the exchange of β-amino amide: **(A)** (retro) aza-Michael addition and **(B)** transamidation via two possible pathways.

While the dissociation of BAA is linked to the reversible nature of Michael nucleophilic addition via the formation of a zwitterionic intermediate after a proton transfer (**Figure 3A**),[39] the transamidation can possibly be enhanced by intramolecular hydrogen bonding between a protonated β-amino group and the amide carbonyl (**Figure 3B-top**). Although direct transamidation begins with a high-enthalpy nucleophilic attack of an amine on the carbonyl carbon,[40] the resulting tetrahedral intermediate is stabilized by an intramolecular hydrogen bond and thus a general acid catalysis, thereby lowering the energy barrier. In β-amino amides, such intramolecular interactions form an entropically favorable, six-membered pseudo-ring via hydrogen bonding,[41] potentially accelerating the transamidation exchange. Interestingly, a benchmark exchange reaction performed on an amide lacking this β-amino group (i.e., n-

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octyloctanamide) also showed a minor conversion to the trans-amidated product after 2h at 160 °C (**Figure S8**). This observation suggests that the effect of hydrogen bonding by a protonated amine moiety, i.e., the general acid catalysis 'charge relay' type acylation mechanism between amide and an additional (partially) protonated amine group, can also facilitate transamidation at elevated temperature. This effect is further enhanced by the proximity of neighboring amino groups in β-amino amides (*vide supra*).

Alternatively, in a scenario that cannot be definitely excluded at this time, the transamidation pathway can possibly also proceed via the formation of a zwitterionic lactam intermediate (**Figure 3B-bottom**). While such lactamization is expected to show a high enthalpic barrier due to the involved ring strain, the intramolecular nucleophilic attack of the β-amino group to a carbonyl carbon could be accelerated through a favorable entropic factor, also known as the neighboring group participation effect.[42–45] The low activation enthalpy seen in the kinetic plots (**Figure 2B**) is thus actually not indicative of such a reversible ring formation scenario, as is the already mentioned slow exchange in simple amides. In an attempt to further probe our mechanistic rationales, we performed studies to force the formation of β-lactam intermediates, but these transient species could not be isolated or observed due to their unstable (short-lived) nature in our various attempts.[46]

Overall, these model studies reveal that the dynamic behavior of BAANs not only arises from the reversible nature of BAA but also from a significant, kinetically comparable transamidation in the presence of β-amino groups. Although free amines are absent in our designated BAA networks, they could be released during BAA dissociation at elevated temperatures and potentially participate in transamidation exchange (*vide supra*).

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Catalytic effects on viscoelasticity of BAAN

Due to the highly endothermic nature of their exchange reactions, most CANs derived from aza-Michael adducts, especially BAAN, require high (re)processing temperatures (typically above 180 °C), implying limitations in terms of energy demand and risk of thermal degradation.[29,47] With the aim to lower this thermal processing window, we therefore sought to exploit catalytic effects on the viscoelastic behavior of BAAN. A series of BAAN were prepared from (2,2,4- and 2,4,4) trimethyl hexamethylenediamine tetra-ester functional crosslinker (**TMH-4E, Figure S9)** and Priamine as illustrated in **Figure 4A**. Various catalysts (5 mol% relative to BAA moieties) were added during network formation, including one organic base (i.e., 1,5,7-triazabicyclo[4.4.0]dec-5-ene, TBD) and three acids (i.e., p-toluenesulfonic acid, pTsOH, methane sulfonic acid, MSA and trifluoromethanesulfonic acid, TfOH). As protonated amines possibly play a role in both exchange pathways (see **Figure 3**), the addition of protic acids could be beneficial for the exchange. Synthetic details are provided in **Section S3**, and the complete cross-linking reactions were confirmed by Fourier-transform infrared spectroscopy (FTIR) (**Figure S10**). The obtained polymer networks are further referred to as N-X, where X is the additional catalyst, and N-Blank refers to the catalyst-free reference network. These networks were shaped into 1-2 mm thick samples via compression molding (180 °C, 3 tons, 30 min) and subsequently subjected to rheological stress relaxation measurements. The relaxation behavior was evaluated using the Kohlrausch–Williams–Watts (KWW) stretched exponential model to construct Arrhenius plots (**Figure S11-15**).

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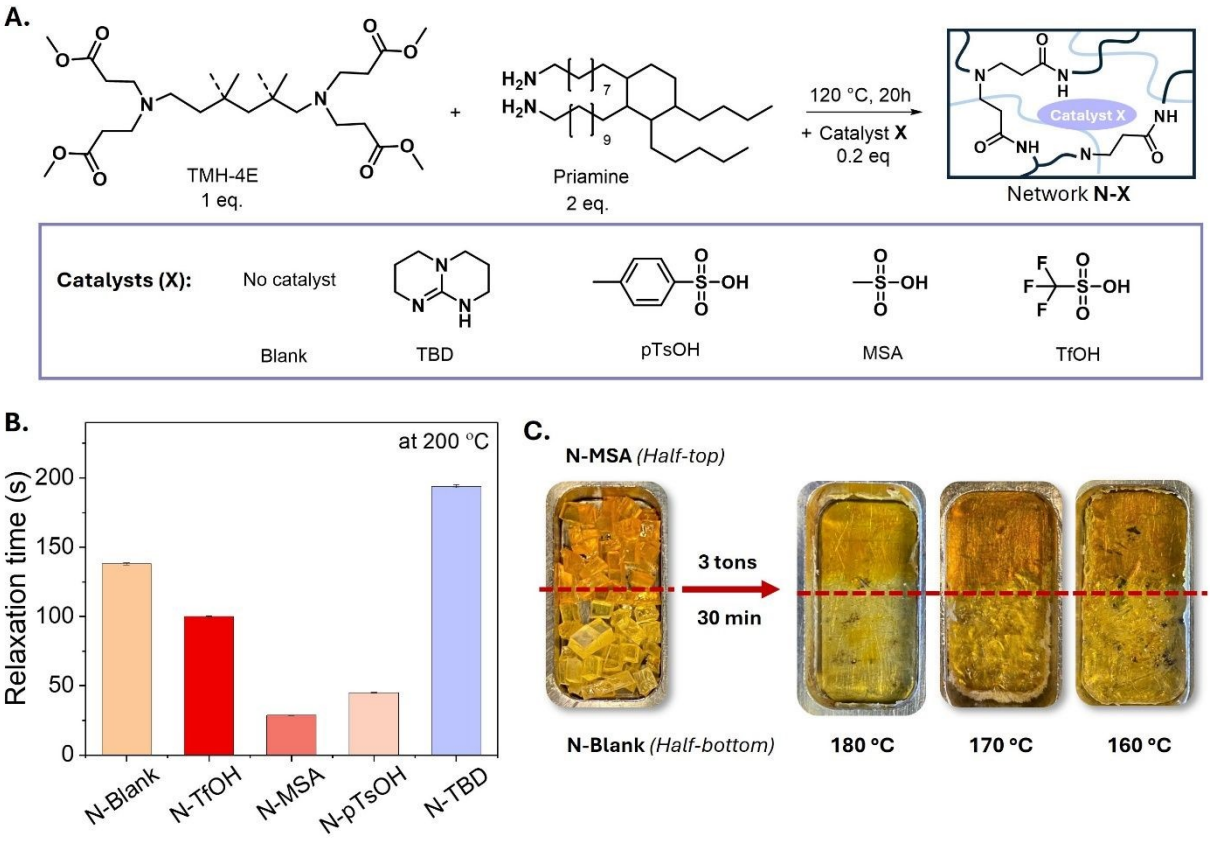

Figure 4. (A) Synthesis of β-amino amide-based dynamic networks prepared using the catalysts displayed in the frame, and **(B)** their relaxation times at 200 °C determined from the KWW stretched exponential model. **(C)** Visualization of the compression molding of N-MSA and N-blank at varying temperatures.

In general, the addition of catalyst(s) linearly shifted the Arrhenius plots to a modified relaxation time (τ), while it maintained the temperature-dependent viscoelasticity (i.e., E_a) comparable to that of the benchmark network (N-Blank) (**Figure S16A**). While all acidic catalysts lower the stress relaxation time (τ), the base TBD hampers BAAN's dynamicity, resulting in slower relaxation profiles, indeed indicating a kinetic role for protonated amine intermediates. More specifically, in comparison to the catalyst-free network N-Blank with τ of 138 s at 200 °C, the addition of 5 mol% TBD into the network resulted in τ of 194 s (**Figure 4B, Figure S16B**). In contrast, the addition

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of an identical molar amount of acidic catalyst significantly accelerated stress relaxation, reducing the relaxation time by more than fourfold for the N-MSA network (τ = 29 s). It should be noted here that the most pronounced acceleration was not observed for the network incorporating the stronger acid TfOH ($pK_a(H_2O) \approx -14$, compared to pK_a (H_2O) ≈ -1.9 for MSA). In fact, this observation is attributed to strong interactions between TfOH and amino moieties in the network, which are known to reduce molecular mobility and thus limit catalytic effectiveness.[48]

As can be observed from the dissociation pathway of BAA (**Figure 3A**), the β-amino group must be protonated to complete the dissociation, although the reversion of BAA is initiated by the deprotonation at the α-carbon position. Therefore, the Brønsted acids here act as proton source, which favors such reversion. On the other hand, the strongly basic catalyst or additive DBU will compete for protons with the amines, thereby reducing the abundance of protonated amines and hampering the exchange process. Moreover, the amines released during BAA dissociation can enable further transamidation exchange, enhancing the overall network dynamicity and stress relaxation behavior. This increased relaxation ability implies improved processability, such as reduced processing time or lower processing temperature. To examine this, the N-Blank and N-MSA networks were cut into small pieces and subjected to the same compression molding process at variable temperatures ranging from 180 to 160 °C. While both samples were fully processable at 180 °C, cut samples of N-Blank failed to heal completely after 30 min at 170 °C (**Figure 4C**). In contrast, N-MSA retained its (re)processability, resulting in homogeneous remolded samples at lower temperatures (160 °C). Notably, although the presence of catalysts might compromise the thermal stability of the materials, no significant impact was observed at the catalyst loading used (5 mol %), as revealed by thermogravimetric analysis of N-MSA and N-Blank (**Figure S17**). This

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demonstrates the enhanced (re)processability of the acid-catalysed CAN, implying beneficial energy savings.

Chemical recycling

At the final stage of this study, it was attempted to chemically degrade the BAANs for the recovery of amino building blocks, which was previously demonstrated in a related BAE platform.[49–51] This chemical degradation process was expected to be enhanced by the double exchange pathway described earlier. The degradation tests were performed on a P-BAAN network, prepared using only Priamine as an amino building block (**Figure S18-19**). The tests were conducted by immersing P-BAAN in an amino compound, either octylamine or ethanolamine, at 140 °C. As shown in **Figure 7A**, depolymerization should involve both possible amine exchange reaction pathways: (*r*etro) aza-Michael *p*athway (*RP*) and/or *t*ransamidation *p*athway (*TP*), in which an additional excess of amines acts as a kinetic trap to enable the recovery of the amino building block of the CANs (Priamine).

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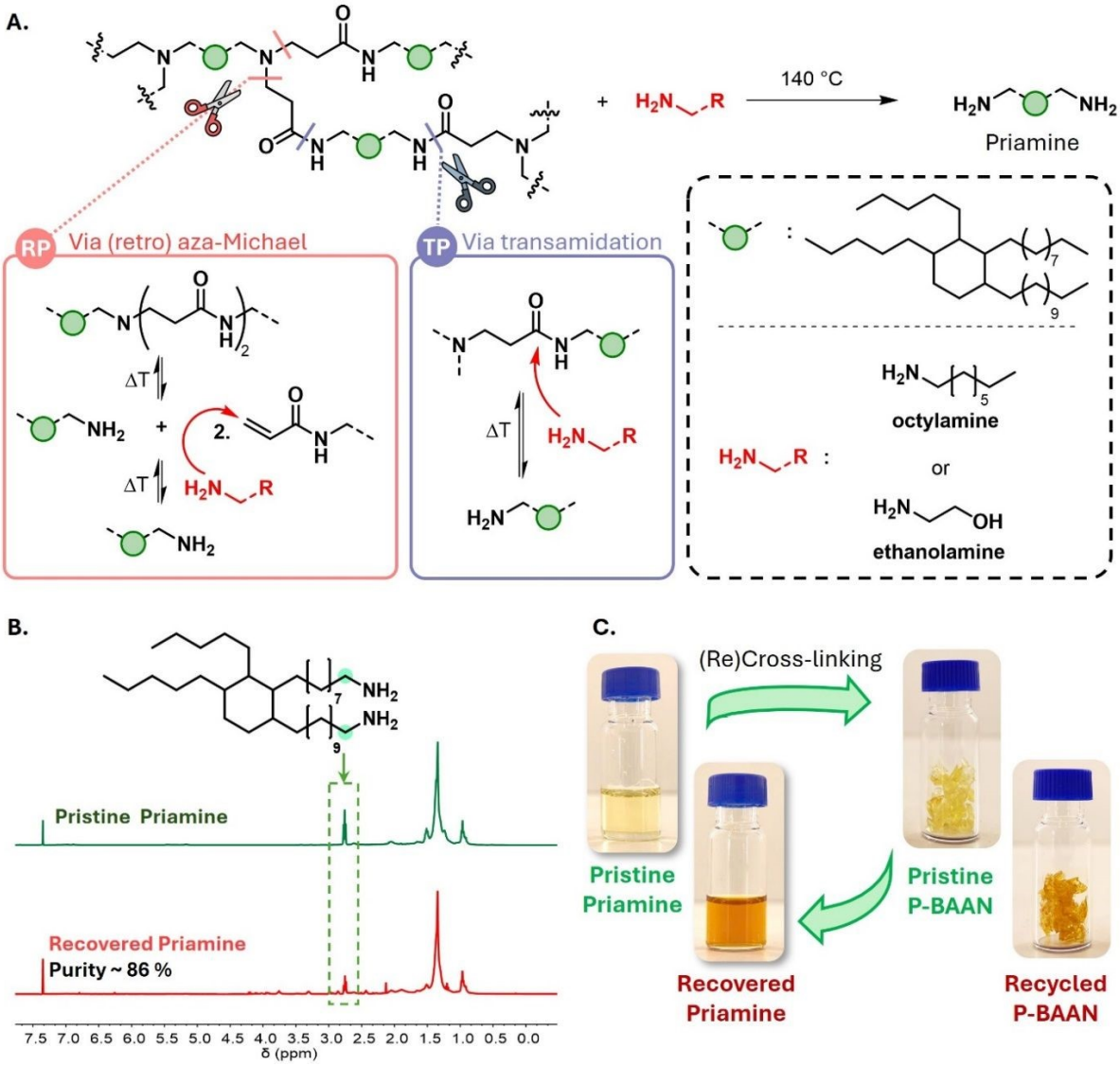

Figure 5. The chemical degradation of the P-BAAN. **(A)** Schematic overview of the network depolymerization pathways; **(B)** Overlayed ^{1}H-NMR spectra of pristine (top) and recovered (bottom) Priamine. **(C)** Visualization of pristine P-BAAN and chemically recycled P-BAAN.

Full dissolution of P-BAAN was observed to be significantly faster when heating was done in ethanolamine (after 2 h at 140 °C) than in octylamine (after 4 h at 140 °C), which could be attributed to the acceleration effect of the (proton-donating) hydroxyl group in ethanolamine (**Figure S20**).[52] Moreover, a benchmark experiment conducted with DMSO as an 'inert' solvent

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did not affect the integrity of the network under identical conditions, even after 24 h at 140 °C (**Figure S21**). To isolate the recovered Priamine, the degraded crude product in ethanolamine was further subjected to DCM-water extraction. Although the dissolution was visualized after 2 h, the depolymerization proceeded at a much longer time scale. Specifically, incomplete depolymerization was observed by matrix-assisted laser desorption/ionization time-of-flight analysis, which primarily detected mono- and di-Michael adducts of Priamine after 3 days (**Figure S22**). The purity of recovered Priamine, assuming Michael adducts as impurities, was quantified by ^{1}H-NMR spectroscopy (**Figure 6**).

After 3 days, Priamine was recovered with 48% purity, which gradually increased over time. After 10 days of depolymerization, a recovery purity of 86% was achieved with a yield of 84 wt.% relative to the total Priamine used for P-BAAN synthesis, in which mono-Michael adduct was the main residual impurity (**Figure 5B** and **Figure S23**). It is recognized that such impurity may potentially influence material properties (e.g., crosslink density), especially over multiple recycling cycles. On the other hand, as a proof of concept, this recovered amino compound was subsequently used as a feedstock to (re)synthesize recycled P-BAAN (**Figure 5C** and **Table 1**).

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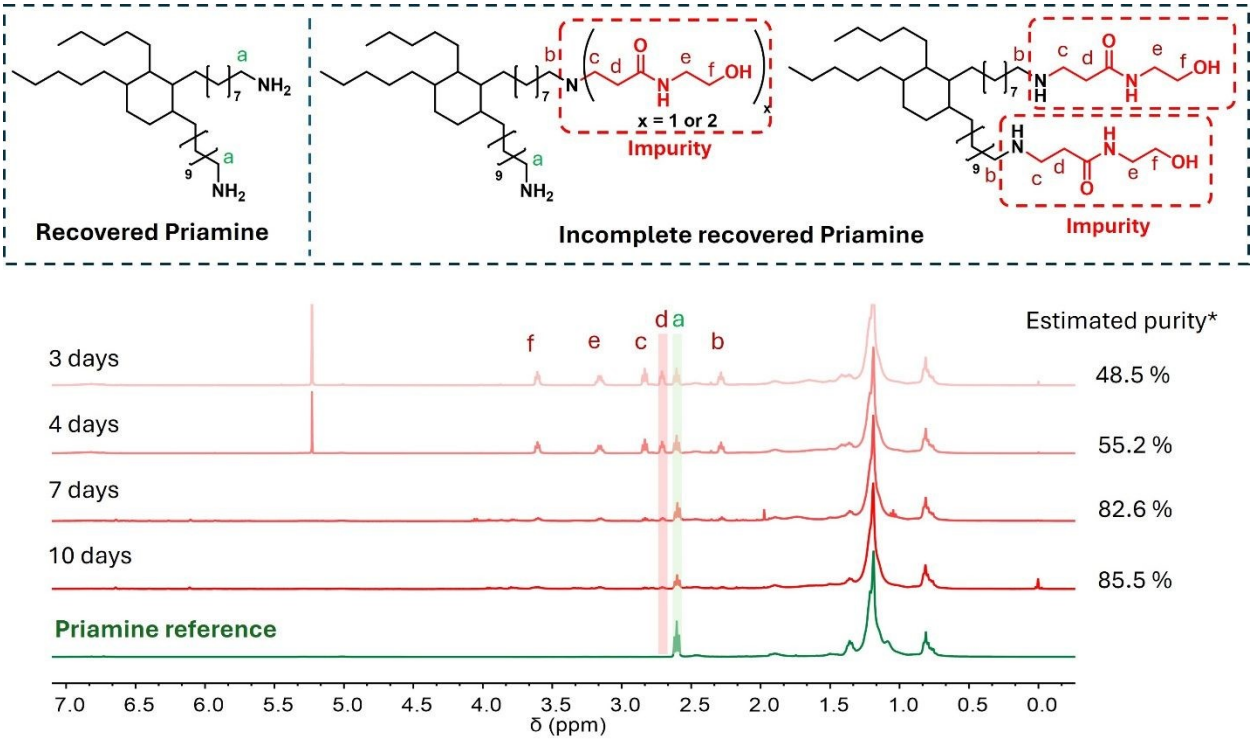

Figure 6. ^{1}H-NMR spectroscopy studies and estimated purities of the degraded crude in ethanolamine (after workup, DCM/H_2O) at different time intervals. The purity was estimated (purity = a/(a + b) x 100%) by considering the Michael adducts as impurities (left structures).

Table 1. Overall properties of the pristine and recycled β-amino amide network.

Samples	T_g [a] (°C)	$T_{d5\%}$ [b] (°C)	$m_{iso180,\ 1h}$ [c] (%)	Swelling degree [d] (%)	Soluble fraction [d] (%)	Modulus (MPa)[e]	ν_e (10^{-3} ·mol·m^{-3})[e]
Pristine P-BAAN	-25	320	1.4	477 ± 09	3.2 ± 2.2	0.286	0.029
Recycled P-BAAN	-26	319	1.2	436 ± 36	4.4 ± 1.9	0.292	0.027

[a] *Determined from DSC analysis with a heating rate of 10 °C.min^{-1}.*

[b] *TGA onset temperatures after 5% weight loss ($T_{d5\%}$) under an air atmosphere.*

[c] *Weight loss after isothermal TGA at 200 °C for 1 hour under an air atmosphere.*

[d] *Swelling degree and soluble fraction obtained from solubility tests in chloroform using at least four samples at room temperature.*

[e] *Storage modulus and cross-link density (ν_e) from dynamic mechanical thermal analysis. ν_e was calculated using the rubber elasticity equation: $E' = 3\nu_eRT$, where R is the gas constant, T is the absolute temperature at Tg + 50 °C.*

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While a brownish coloration and slightly increased soluble fraction (attributed to residual impurities) were observed, the recycled P-BAAN showed desirable chemical characteristics comparable to pristine P-BAAN, as shown using FTIR spectroscopy analysis (**Figure S24**). Moreover, the chemically recycled P-BAAN largely retained its thermal and thermomechanical properties (**Figure S25-28**), highlighting the potential for the chemical recycling of BAA-derived CANs.

Conclusion

In summary, this work has elucidated the bond exchange kinetics and further reveals an interesting transamidation exchange pathway in β-amino amides. Catalyst screening highlights the advantage of using acidic catalysis for the acceleration of stress relaxation and consequently enhancing processability, and points toward mechanisms that involve protonated amine species. Notably, the addition of 5 mol% methane sulfonic acid enables the obtained β-amino amide network to relax applied stress up to four times faster at 200 °C, while extending the processability window in comparison to the catalyst-free network. Furthermore, capitalizing on the finding of dual amine exchange reactions on BAAs, the chemical recycling of the amino building block (Priamine) from the cross-linked material was demonstrated. Priamine could be restored with a purity of 86% and a yield of 84 wt.%, which was successfully employed to resynthesize CANs without significant changes in chemical and thermal properties. The findings in this study not only expand the mechanistic understanding of β-amino amide dynamic chemistry but also establish a more practical route toward recyclable, high-performance thermosets.

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Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the Supplementary Information. Supplementary Information is available at https://doi.org/DOI.

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