Supplementary Information (SI) for Polymer Chemistry.
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Supporting information: Polyurethane foam acidolysis with carboxylic acids: acid structure dictates N-containing product distribution and kinetics

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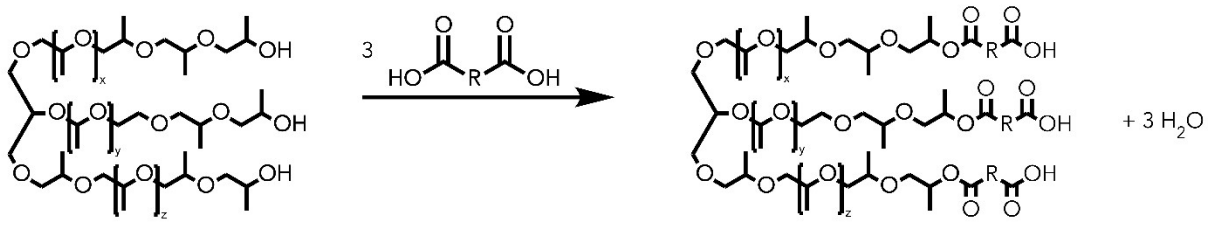
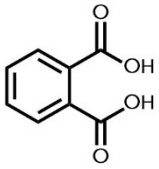
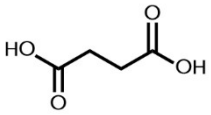
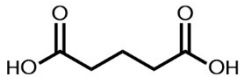
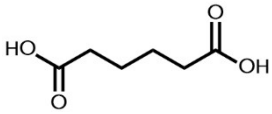
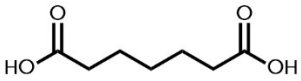
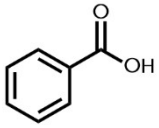


Figure S1: Stoichiometry for esterification of polyol with excess dicarboxylic acid to form a polyol ester and water.

Table S1: Carboxylic and dicarboxylic acids selected for study of PUF acidolysis & relevant physical properties.

Name	Chemical Structure	Mol. Weight (g/mol)	T_m (°C) [1]
Phthalic acid (PA)		166.1	207
Succinic acid (SA)		118.1	185
Glutaric acid (GA)		132.1	98
Adipic acid (AA)		146.1	152
Pimelic acid (PiA)		160.2	105
Benzoic acid (BA)		122.1	122

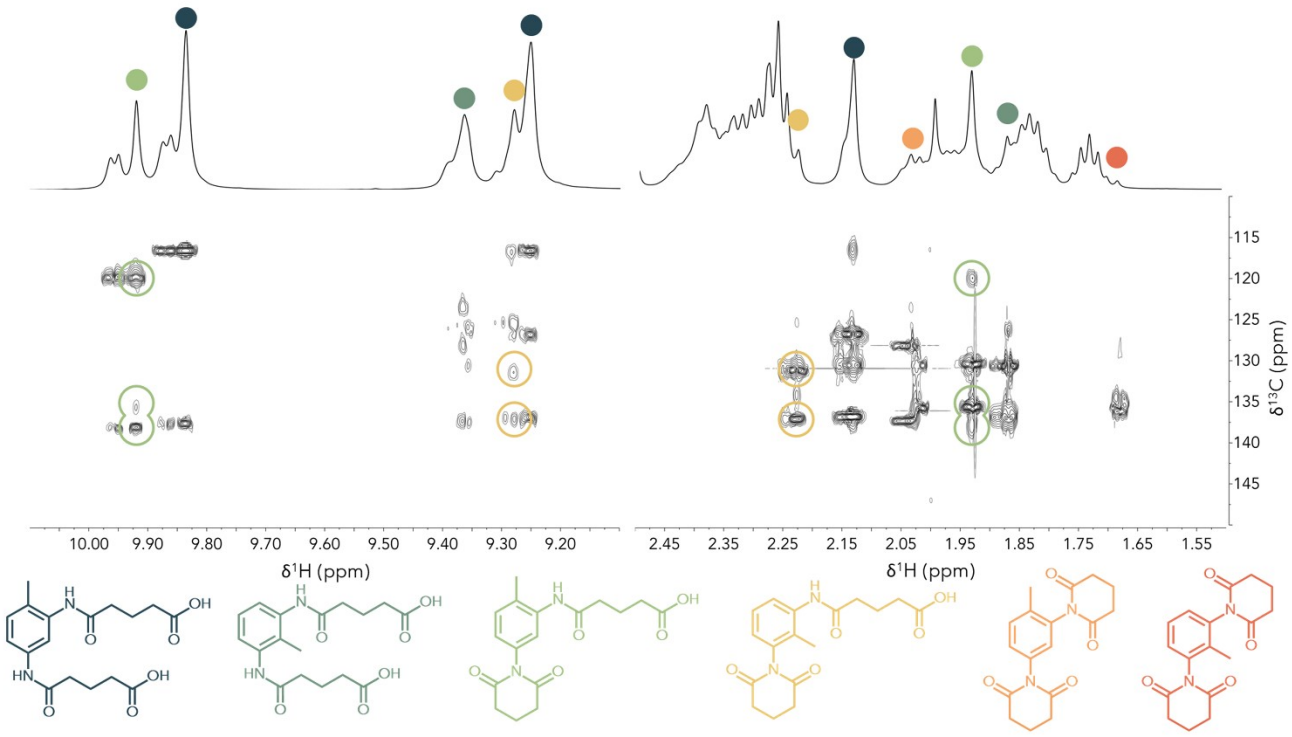


Figure S2: ^{1}H-^{13}C HMBC NMR spectrum of isolated amides/imides from PUF acidolysis with GA with key assignments. Intermediate assignments were made by comparing the amide region to the methyl region. Reaction conditions: 3 g M-PUF, 3 g GA, 185 °C, 4 hours under an inert (N_2) atmosphere.

Assignment of NMR peaks of reaction products from M-PUF acidolysis with GA

Peak assignments were initially made using the kinetic experiments detailed in the main text (see Figures S21-S23). The methyl region (δ^1H = 1.5 – 2.5 ppm) and amide region (δ^1H = 9.1 – 10.1 ppm) were the most useful regions of the ^{1}H NMR for making assignments. Based solely on time-dependent analysis from kinetic experiments and the known ratio of [2,4-TDI] : [2,6-TDI] = 4 : 1 in the foam formulation, most peaks could be assigned. Peaks decreasing in magnitude as the reaction proceeded were assigned to diamides, while peaks increasing in magnitude as the reaction proceeded were assigned to diimides. Peaks at δ^1H = 2.10, 9.19 and 9.76 were assigned to GA-2,4-AA, and the peaks at δ^1H = 1.84 and 9.30 were assigned to GA-2,6-AA. Diimides lack direct N-H bonds and thus only have methyl signals; peaks at δ^1H = 1.99 and 1.65 were assigned to GA-2,4-II and GA-2,6-II, respectively.

Two amide peaks (δ^1H = 9.22 and 9.85 ppm) and two methyl peaks (δ^1H = 1.90 and 2.20) initially increased, then decreased, and were therefore assigned to amide-imide intermediates; however, ^{1}H NMR does not contain enough information to deduce which two of three possible

intermediates (GA-2,4-AI, GA-2,4-IA, GA-2,6-AI) corresponded to which peak. Furthermore, it was not immediately clear which peak assigned to GA-2,4-AA was associated with the 2-amide and which was the 4-amide.

To determine which intermediates were formed during the reaction, the N-containing products of a GA acidolysis reaction were isolated (see Experimental Section for details) and analyzed via ^{1}H NMR, ^{1}H-^{13}C HMBC NMR, and ^{1}H-^{15}N HMBC NMR. It is important to note that isolation of products changed their chemical environment slightly, and peak locations reported for ^{1}H NMR of kinetic experiments may differ by ca. 0.05 – 0.1 ppm from the NMR of the isolated products. In addition, several additional amide peaks appear that are not visible in the kinetic experiments; we attribute these to acid-bridged dimeric amide species and hypothesize that their greater concentration in the isolated products is due to their lower solubility in EtOAc than their respective monomers. ^{1}H-^{13}C HMBC NMR was particularly useful, as the aromatic region of the ^{13}C axis of the ^{1}H-^{13}C HMBC NMR (δ^{13}C = 120 – 150 ppm) could be used to find carbons proximal to amide -NH and methyl -CH_3 signals. Notably, amide groups in the 2- and 6- positions should share 2-3 aromatic cross peaks with the methyl in the 1-position, while amide groups in the 4-position should have aromatic cross peaks only with carbons 4-5 bonds away from the methyl -CH_3. Thus, amides in the 2-position can be differentiated from amides in the 4-position via ^{1}H-^{13}C HMBC NMR.

For example, the peak at δ^{1}H = 9.19 ppm assigned to GA-2,4-AA has cross peaks at δ^{13}C = 116.4, 126.8, and 137.0 ppm. The methyl peak of GA-2,4-AA at δ^{1}H = 2.10 ppm has cross peaks at δ^{13}C = 116.4, 126.8, 130.5, and 136.9 ppm. Because these two signals share three aromatic cross peaks, it is apparent that the peak at δ^{1}H = 9.19 ppm corresponds to the amide in the 2-position (*para*-). In contrast, the other amide peak of GA-2,4-AA (δ^{1}H = 9.76 ppm) has cross peaks at 116.5 and 137.6 ppm. The lack of overlap in cross signals between this peak and the methyl peak suggests that the signal at δ^{1}H = 9.76 ppm corresponds to the 4-amide (*ortho*-).

A similar analysis was applied to the reaction intermediates. It is apparent from the high concentration observed during kinetic reactions that the signals at δ^{1}H = 1.90 and 9.85 ppm correspond to the main intermediate formed, and must therefore correspond to a GA-2,4 species. Both peaks had aromatic cross peaks at δ^{13}C = 119.9, 135.8, and 138.0 ppm (Figure S2, green circled cross peaks), indicating that the amide in this intermediate was in the 2-position. We thus assign these signals to GA-2,4-AI. Similarly, both signals of the minor intermediate (δ^{1}H = 2.20 & 9.22 ppm) had aromatic cross peaks at δ^{13}C = 125.4, 131.3, and 137.1 ppm (Figure S2, yellow circled cross peaks), indicating that the amide signal at δ^{1}H = 9.22 ppm also corresponded to an amide in the 2-position. These signals were thus assigned to GA-2,6-AI.

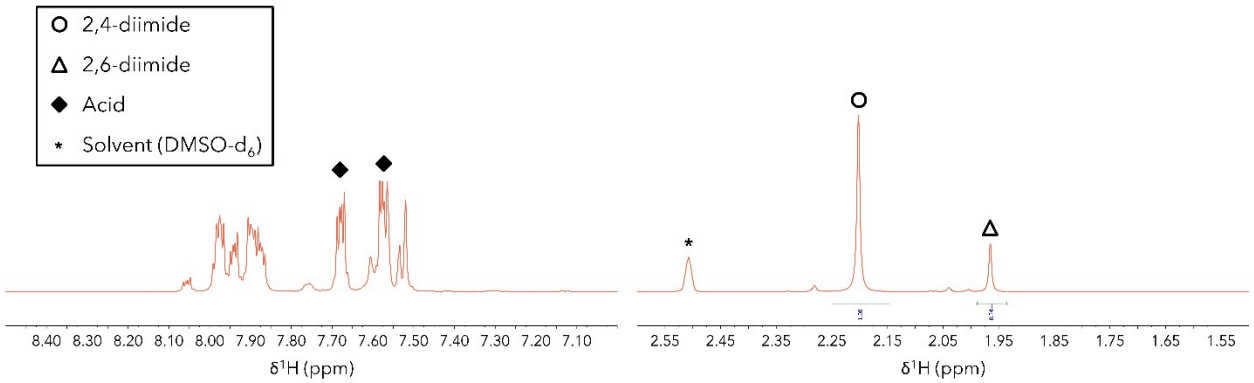


Figure S3: ^{1}H NMR of products from acidolysis with PA, showing the formation of diimide products. The aromatic region was difficult to analyze for PA due to overlapping signals of PA and phthalic anhydride (PAnh) and is therefore not labelled here beyond identification of the acid. Reaction conditions: 0.5 g M-PUF, 1.5 g PA, 195 °C, 2 hours under an inert (N_2) atmosphere.

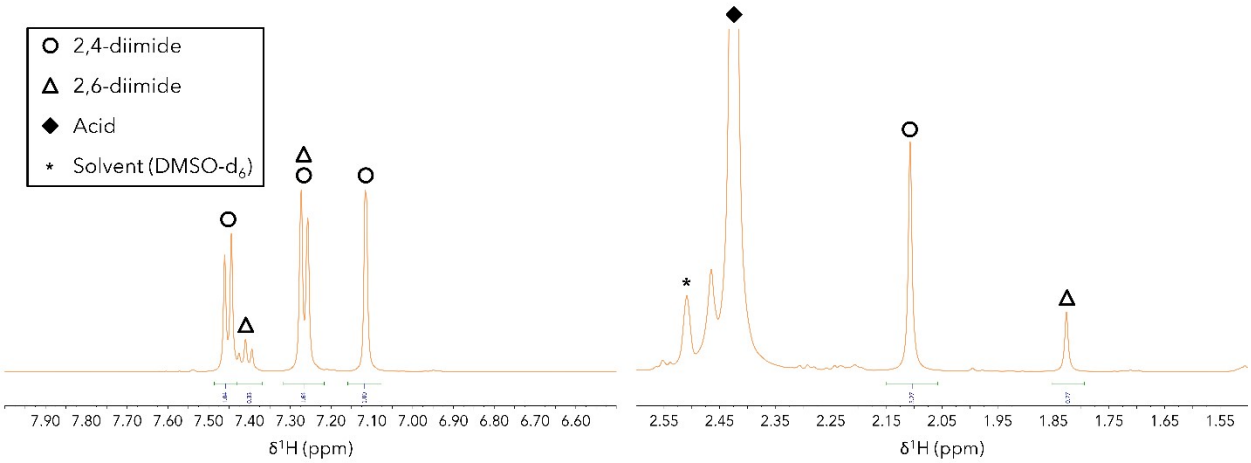


Figure S4: ^{1}H NMR of products from acidolysis with SA, showing the formation of diimide products. Reaction conditions: 0.5 g M-PUF, 1.5 g SA, 195 °C, 2 hours under an inert (N_2) atmosphere.

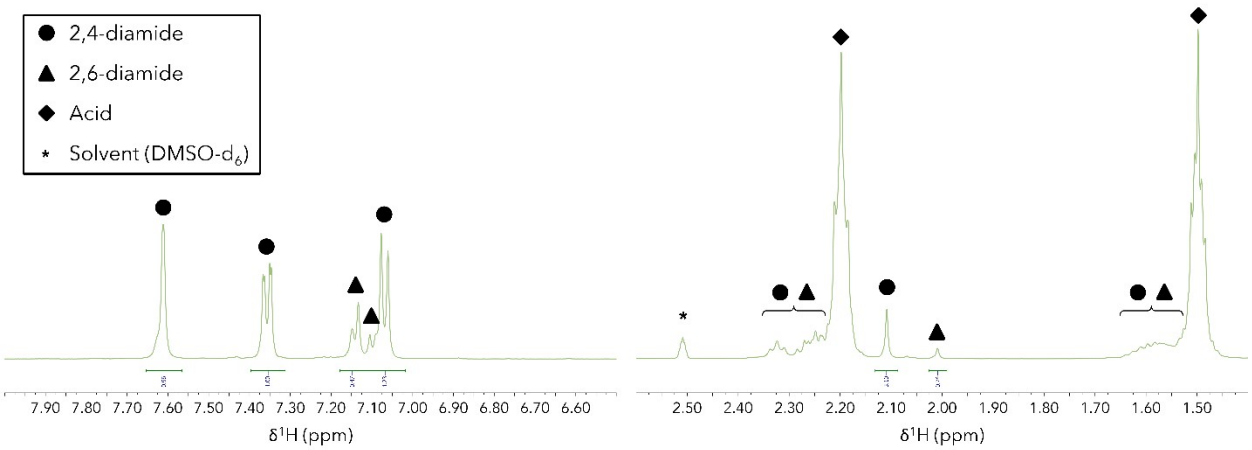


Figure S5: ^{1}H NMR of products from acidolysis with AA, showing the formation of diamide products. Reaction conditions: 0.5 g M-PUF, 1.5 g AA, 195 °C, 2 hours under an inert (N_2) atmosphere.

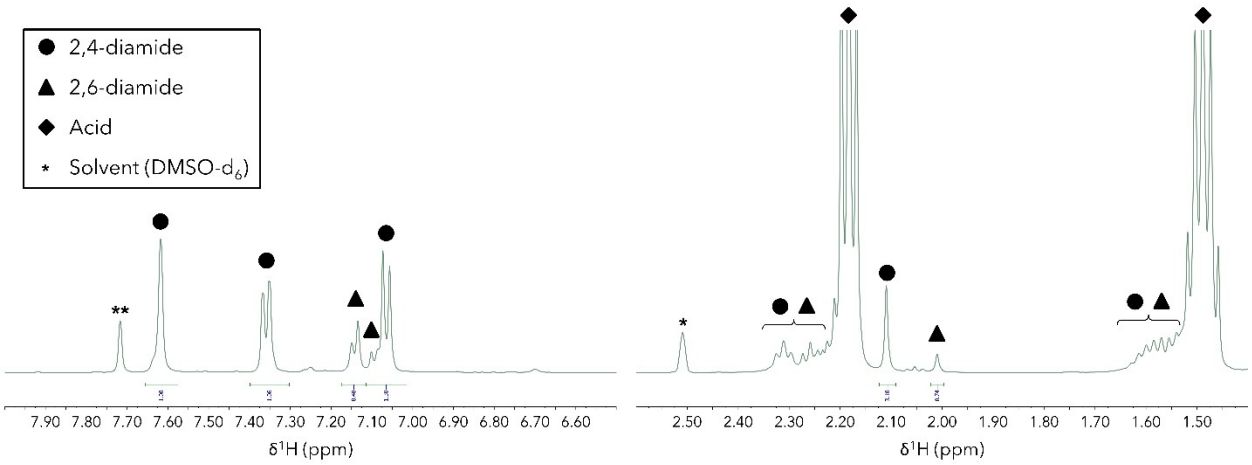


Figure S6: ^{1}H NMR of products from acidolysis with PiA, showing the formation of diamide products. The peak marked ** is an impurity from the PiA used and is unrelated to the acidolysis reaction. Reaction conditions: 0.5 g M-PUF, 1.5 g PiA, 195 °C, 2 hours under an inert (N_2) atmosphere.

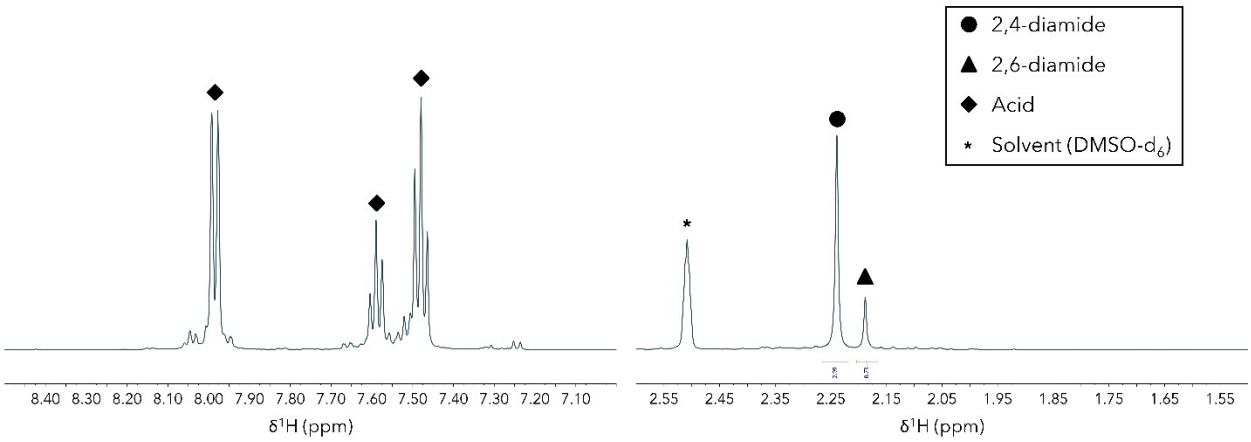


Figure S7: ^{1}H NMR of products from acidolysis with BA, showing the formation of diamide products. The aromatic region was difficult to analyze for BA due to overlapping signals of BA and is therefore not labelled here beyond identification of the acid. Reaction conditions: 0.5 g M-PUF, 1.5 g BA, 195 °C, 24 hours under an inert (N_2) atmosphere.

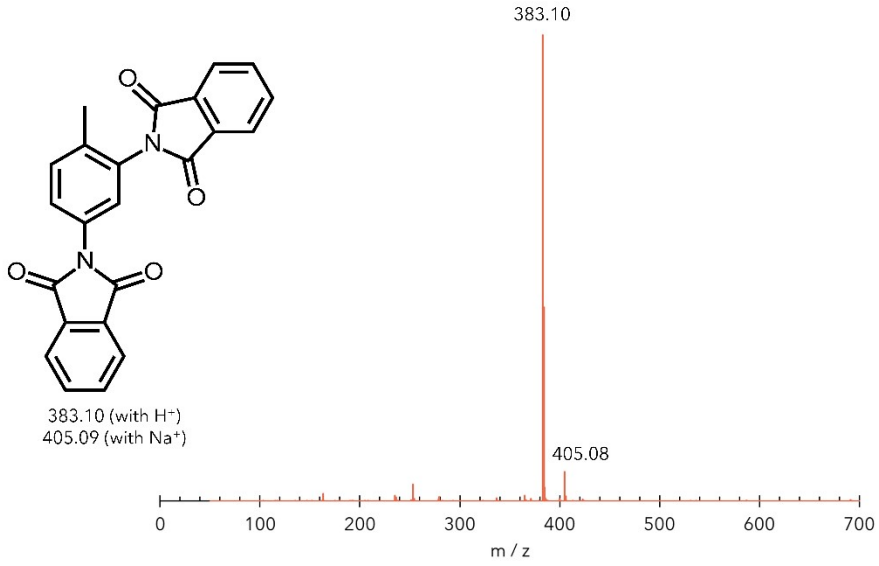


Figure S8: Full UPLC-MS of products from M-PUF acidolysis with PA, along with key assignments. Reaction conditions: 0.5 g M-PUF, 1.5 g PA, 195 °C, 2 hours under an inert (N_2) environment.

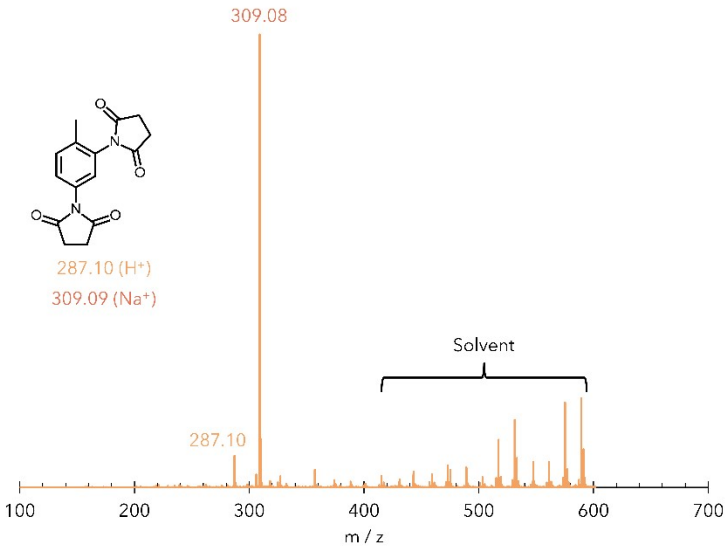


Figure S9: Full UPLC-MS of products from M-PUF acidolysis with SA, along with key assignments. Reaction conditions: 0.5 g M-PUF, 1.5 g SA, 195 °C, 2 hours under an inert (N_2) environment.

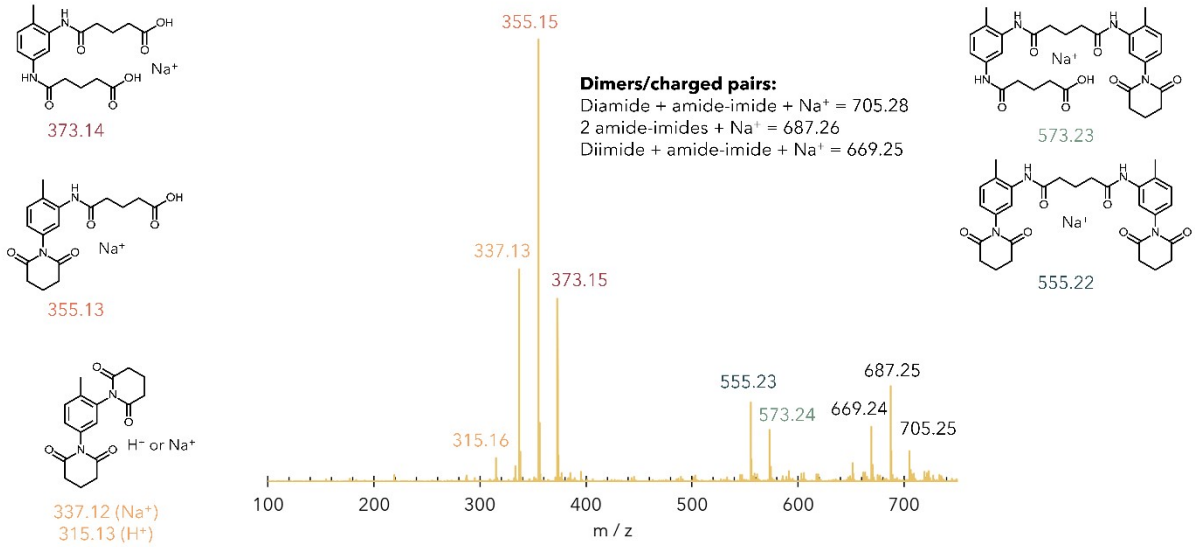


Figure S10: Full UPLC-MS of products from M-PUF acidolysis with GA, along with key assignments. Reaction conditions: 0.5 g M-PUF, 1.5 g GA, 195 °C, 2 hours under an inert (N_2) environment.

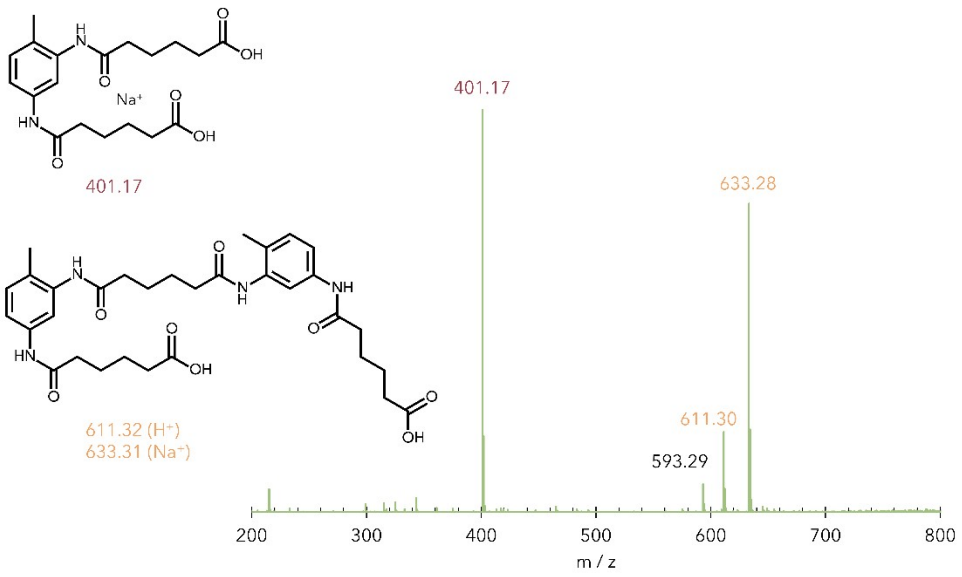


Figure S11: Full UPLC-MS of products from M-PUF acidolysis with AA, along with key assignments. Reaction conditions: 0.5 g M-PUF, 1.5 g AA, 195 °C, 2 hours under an inert (N_2) environment.

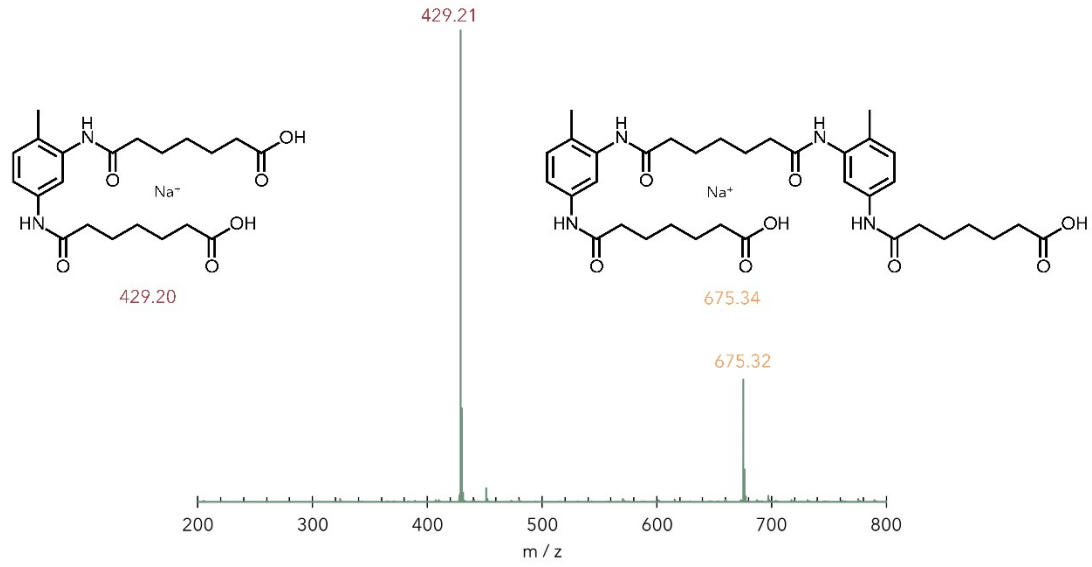


Figure S12: Full UPLC-MS of products from M-PUF acidolysis with PiA, along with key assignments. Reaction conditions: 0.5 g M-PUF, 1.5 g PiA, 195 °C, 2 hours under an inert (N_2) environment.

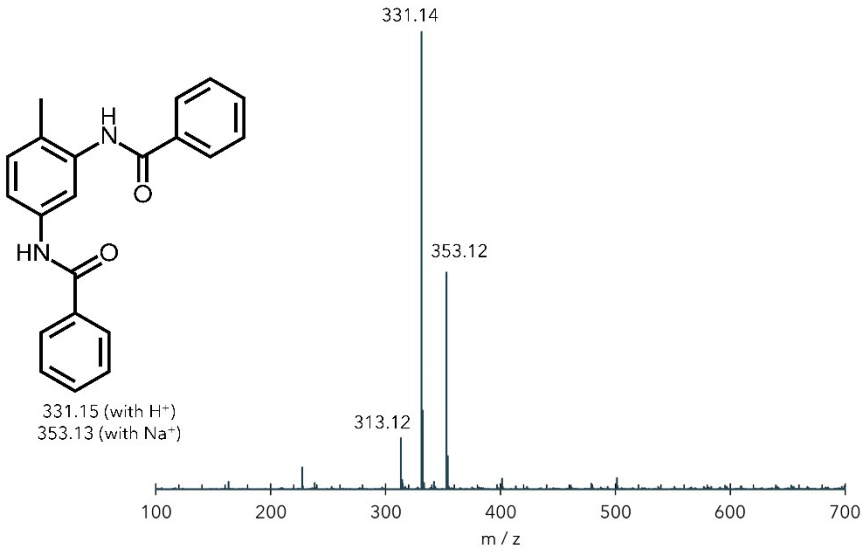


Figure S13: Full UPLC-MS of products from M-PUF acidolysis with BA, along with key assignments. Reaction conditions: 0.5 g M-PUF, 1.5 g BA, 195 °C, 24 hours under an inert (N_2) environment.

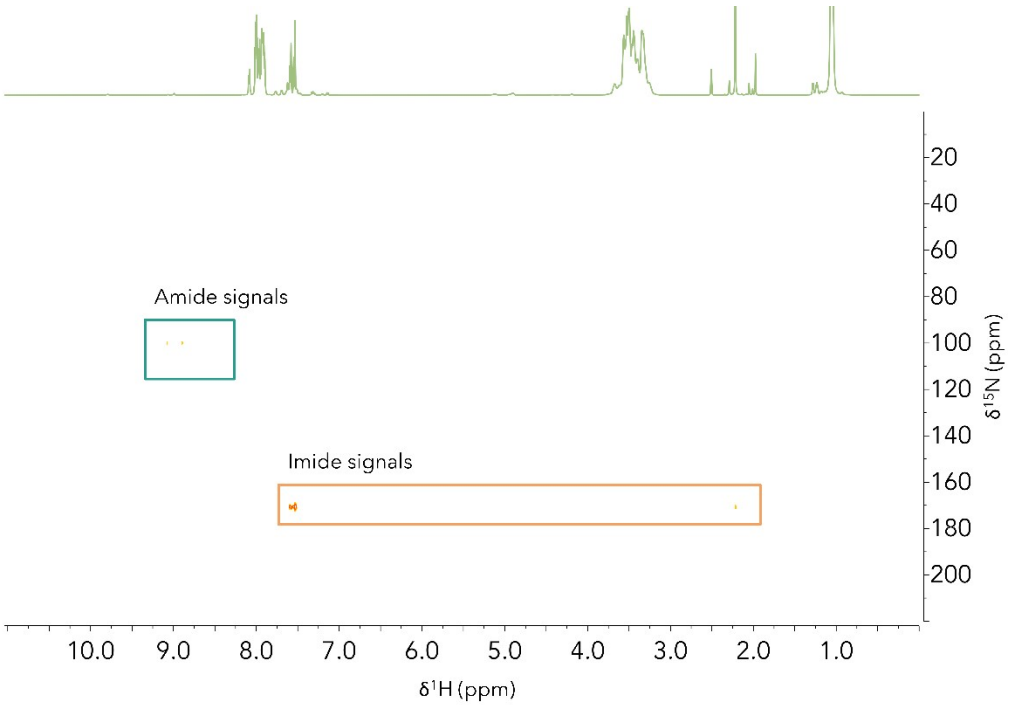


Figure S14: ^{1}H – ^{15}N HMBC NMR of reaction mixture from M-PUF acidolysis with PA. Reaction conditions: 0.5 g M-PUF, 375 mg PA*, 195 °C, 2 hours under inert (N_2) atmosphere. NMR sample: 150 mg products (taken without separations), 600 µL DMSO-d_6. *While the products using 1.5 g PA were the same, a reaction with lower PA loading had to be run to

perform ^{1}H-^{15}N HMBC NMR to prevent signals from PA in the aromatic region from interfering with analysis of the spectrum.

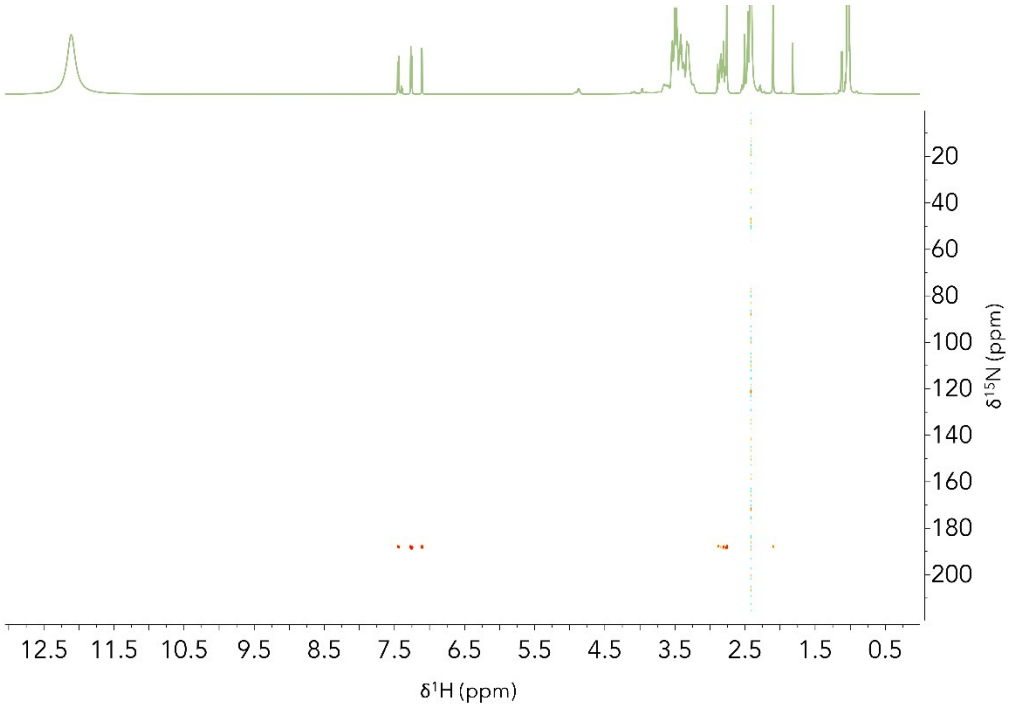


Figure S15: ^{1}H – ^{15}N HMBC NMR of reaction mixture from M-PUF acidolysis with SA. Reaction conditions: 0.5 g M-PUF, 1.5 g SA, 165 °C, 25 minutes under inert (N_2) atmosphere. NMR sample: 150 mg products (taken without separations), 600 µL DMSO-d_6.

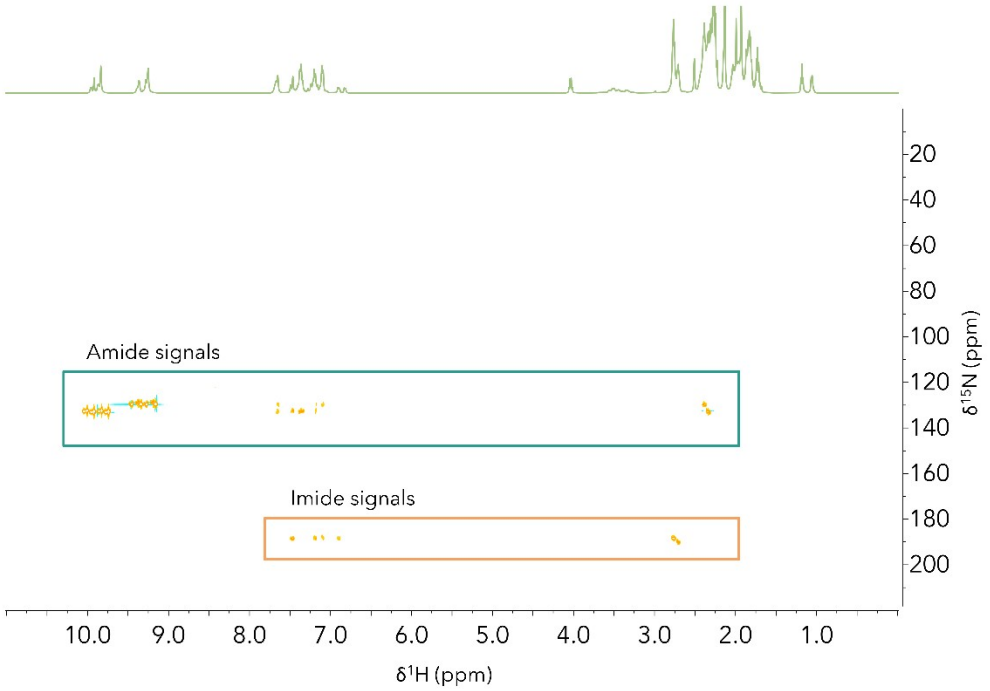


Figure S16: ^{1}H – ^{15}N HMBC NMR of isolated amides/imides extracted from M-PUF acidolysis with GA. Reaction conditions: 3 g M-PUF, 3 g GA, 185 °C, 4 hours under inert (N_2) atmosphere. NMR sample: 100 mg amides, 600 µL DMSO-d_6.

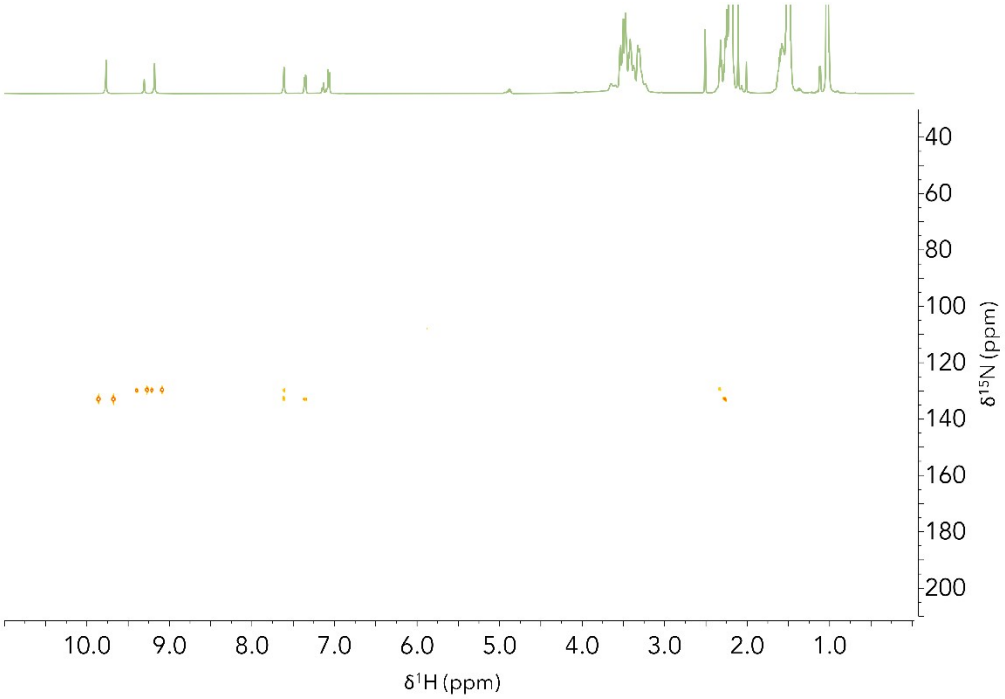


Figure S17: ^{1}H – ^{15}N HMBC NMR of reaction mixture from M-PUF acidolysis with AA. Reaction conditions: 0.5 g M-PUF, 1.5 g AA, 195 °C, 2 hours under inert (N_2) atmosphere. NMR sample: 150 mg products (taken without separations), 600 µL DMSO-d_6. Only amides were detected in the product mixture.

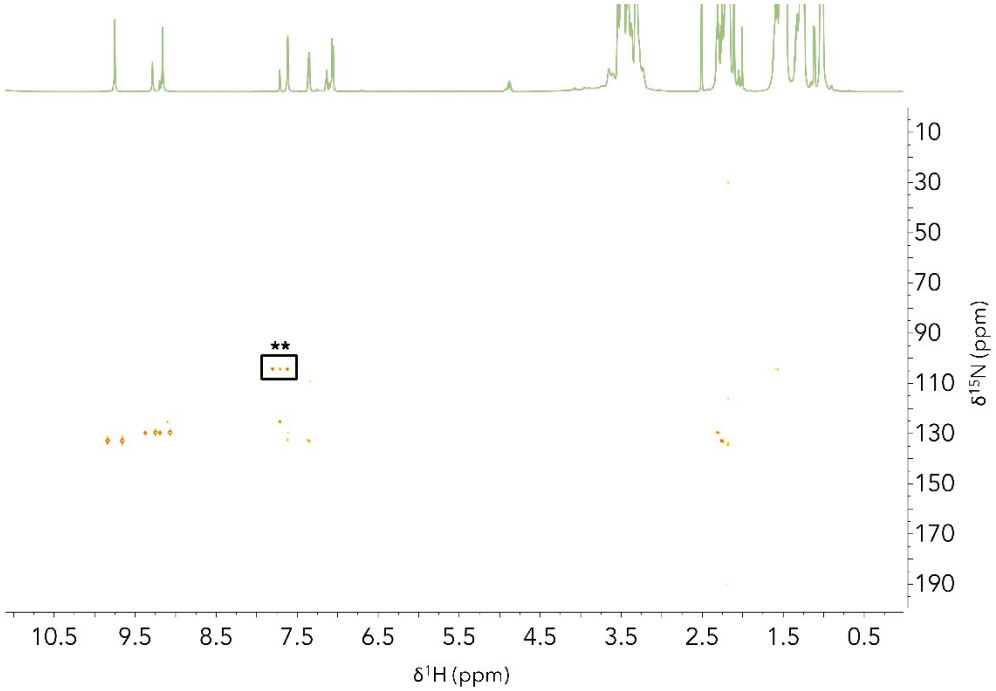


Figure S18: ^{1}H – ^{15}N HMBC NMR of reaction mixture from M-PUF acidolysis with PiA. Reaction conditions: 0.5 g M-PUF, 1.5 g PiA, 195 °C, 2 hours under inert (N_2) atmosphere. NMR sample: 150 mg products (taken without separations), 600 µL DMSO-d_6. Only amides were detected in the product mixture. Signals marked ** are contaminants found in the PiA used and are not believed to be related to the acidolysis reaction.

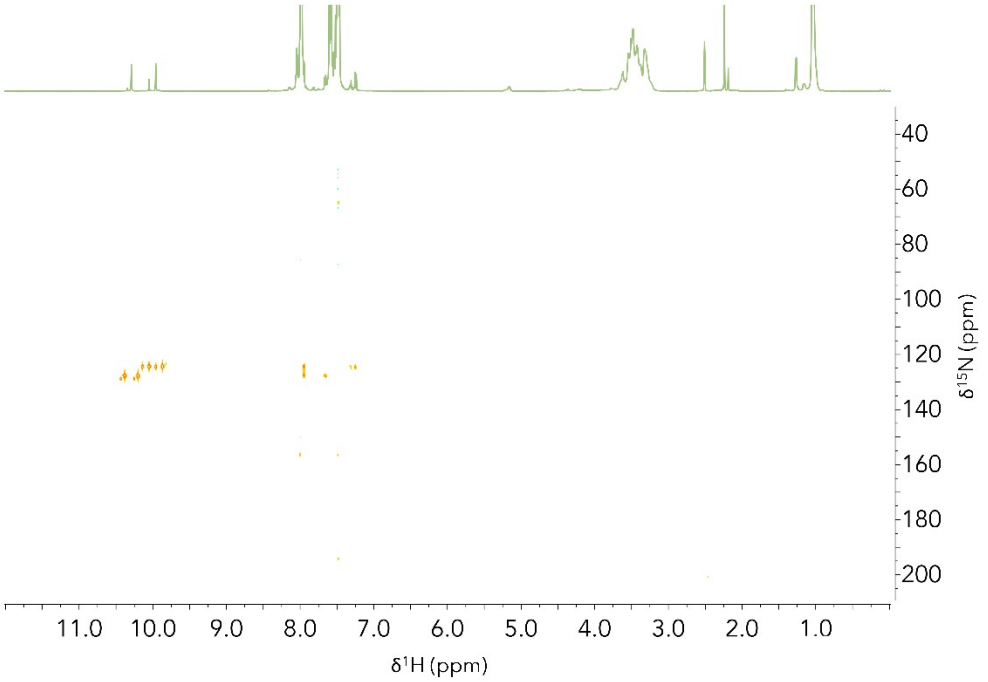
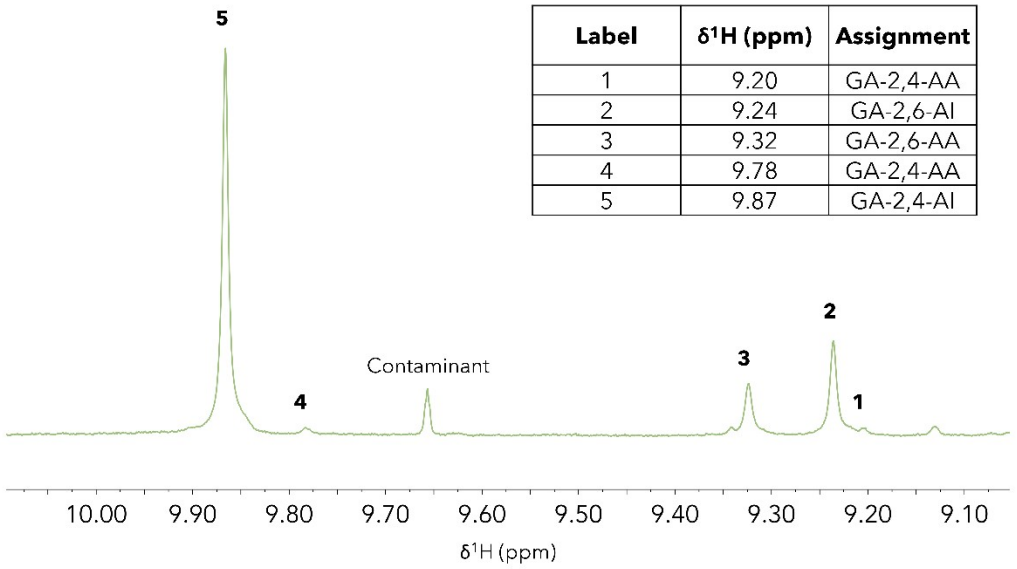


Figure S19: ^{1}H – ^{15}N HMBC NMR of reaction mixture from M-PUF acidolysis with BA. Reaction conditions: 0.5 g M-PUF, 1.5 g BA, 195 °C, 24 hours under inert (N_2) atmosphere. NMR sample: 150 mg products (taken without separations), 600 µL DMSO-d_6. Only amides were detected in the product mixture.



Label	δ¹H (ppm)	Assignment
1	9.20	GA-2,4-AA
2	9.24	GA-2,6-AI
3	9.32	GA-2,6-AA
4	9.78	GA-2,4-AA
5	9.87	GA-2,4-AI

Figure S20: ^{1}H NMR of reaction mixture from a long (120 hour) M-PUF acidolysis with GA. Reaction conditions: 0.5 g M-PUF, 1.5 g GA, 195 °C, 120 hours under inert (N_2) atmosphere. NMR sample: 150 mg products (taken without separations), 25 mg MA (internal standard), 600 µL DMSO-d_6.

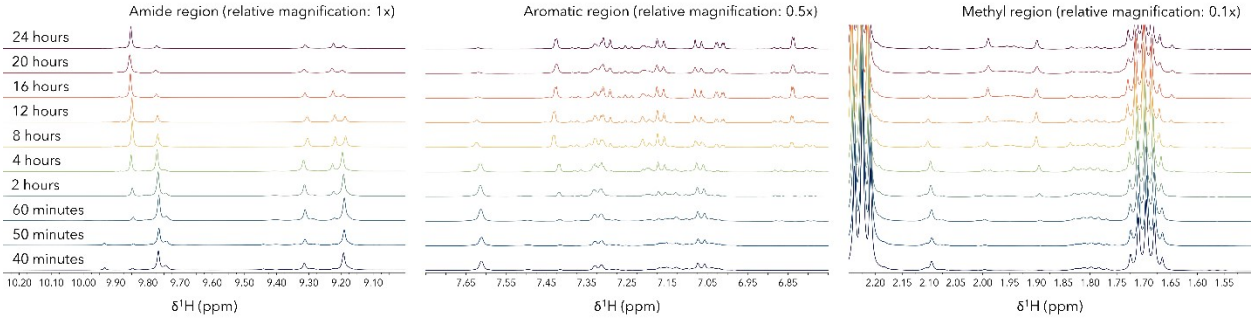


Figure S21: ^{1}H NMR of M-PUF acidolysis with GA at 165 °C and increasing reaction times. Reaction conditions: 0.5 g M-PUF, 1.5 g GA, 165 °C, 40 minutes – 24 hours under an inert (N_2) atmosphere. NMR samples: 150 mg products, 25 mg MA (internal standard), 600 µL DMSO-d_6.

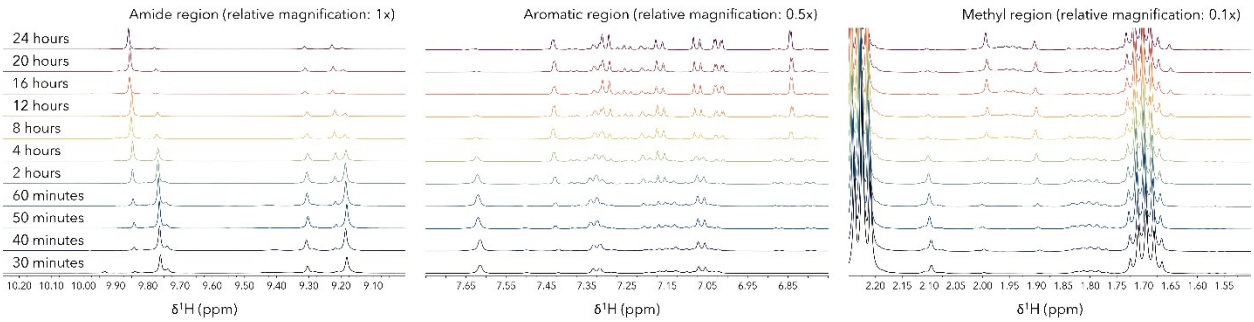


Figure S22: ^{1}H NMR of M-PUF acidolysis with GA at 175 °C and increasing reaction times. Reaction conditions: 0.5 g M-PUF, 1.5 g GA, 175 °C, 30 minutes – 24 hours under an inert (N_2) atmosphere. NMR samples: 150 mg products, 25 mg MA (internal standard), 600 µL DMSO-d_6.

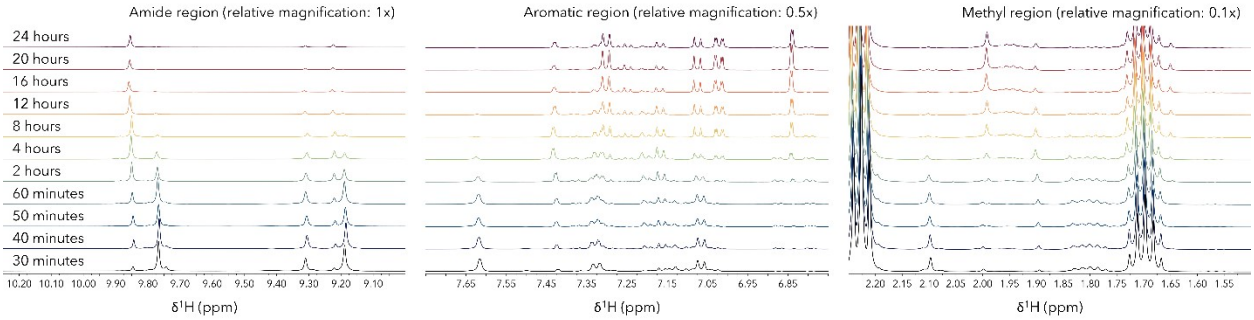


Figure S23: ^{1}H NMR of M-PUF acidolysis with GA at 185 °C and increasing reaction times. Reaction conditions: 0.5 g M-PUF, 1.5 g GA, 185 °C, 30 minutes – 24 hours under an inert (N_2) atmosphere. NMR samples: 150 mg products, 25 mg MA (internal standard), 600 µL DMSO-d_6.

Kinetic modeling of imide formation during acidolysis

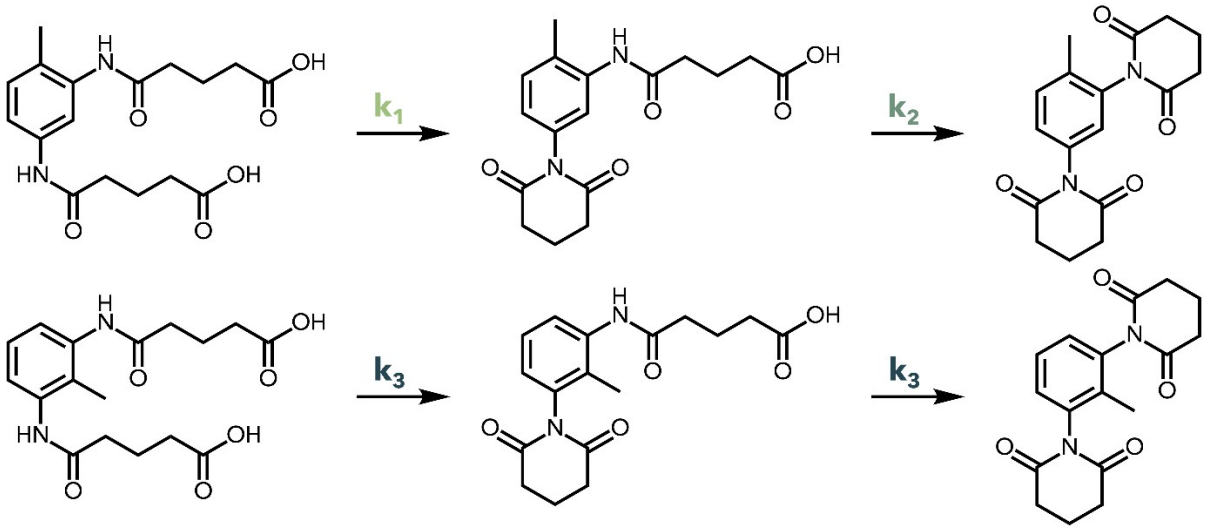
The kinetic models were derived based on previously understood knowledge regarding the kinetics of PUF acidolysis.[2] Polyurethane acidolysis proceeds via the following stoichiometry:

$$\text{Urethane} + \text{DCA} \rightarrow \text{Polyol} + \text{Amide} + CO_2$$

$$\text{Urea} + 2\ \text{DCA} \rightarrow 2\ \text{Amide} + CO_2 + H_2O$$

Previous work has demonstrated that polyol/amide release is the rate-limiting step during urethane/urea bond decomposition, and therefore CO_2 evolution is a good proxy for the release of amides during the reaction.[2] As a result, upon cessation of CO_2 evolution it is a good assumption that amide species are no longer being generated. Data to measure the kinetics of imide formation from amides were therefore only included in the model after cessation of CO_2

evolution so that the kinetic model did not need to include rate expressions for amide generation. For GA acidolysis, this was after 120 minutes at 165 °C, 50 minutes at 175 °C, and 40 minutes at 185 °C; for SA acidolysis, this was after 25 minutes at 165 °C and after 10 minutes at 175 °C & 185 °C.



Scheme S1: simplified kinetic model for imide formation during M-PUF acidolysis with GA in which the pathway to form GA-2,4-IA is excluded.

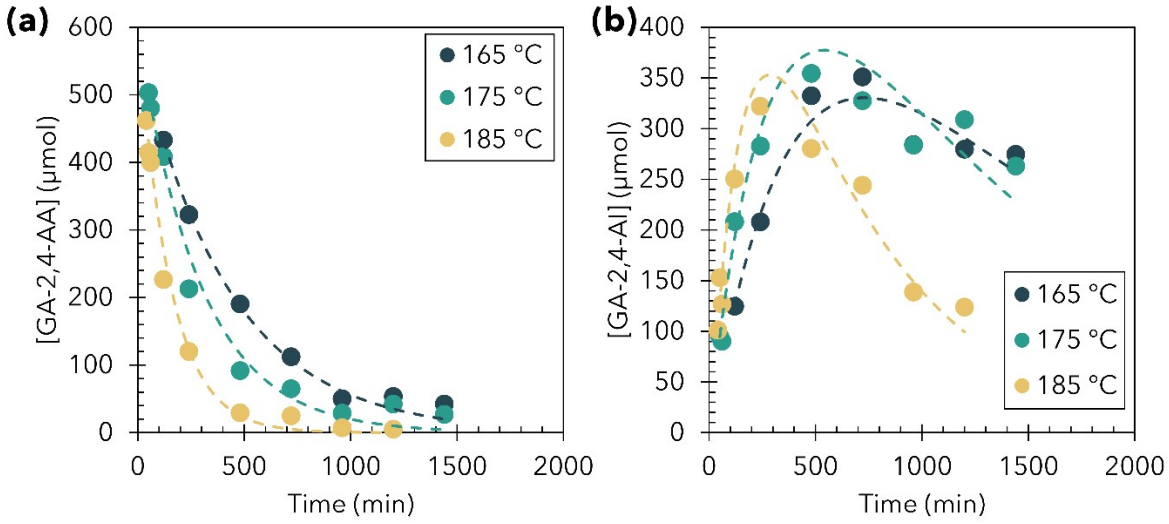


Figure S24: NMR data (dots) and simplified kinetic model fits (dashed lines) for species formed in the reaction mixture after M-PUF acidolysis with GA: **(a)** GA-2,4-AA, **(b)** GA-2,4-AI using the model detailed in Scheme S1. Reaction conditions: 0.5 g M-PUF, 1.5 g GA, 30 minutes – 24 hours at 165 – 185 °C under an inert (N_2) atmosphere.

Table S2: Tabulated kinetic parameters for simplified kinetic model of M-PUF acidolysis with GA*†°

T (°C)	k_1 (min^{-1})	k_2 (min^{-1})
165	2.1E-03 ± 1.9E-05	4.9E-04 ± 4.9E-06
175	3.2E-03 ± 2.3E-05	1.7E-03 ± 4.0E-06
185	6.2E-03 ± 5.6E-05	3.4E-03 ± 8.4E-06
E_a (kJ/mol)	91 ± 14	91 ± 28
lnA	19 ± 4	17 ± 7

*Values correspond to kinetic model shown in Scheme S1.

†Error values for rate constants represent 95% confidence intervals; error values for E_a and lnA represent standard errors.

°Values for k_3 are not affected by the exclusion of GA-2,4-IA in the model and are the same as reported below in Table S3.

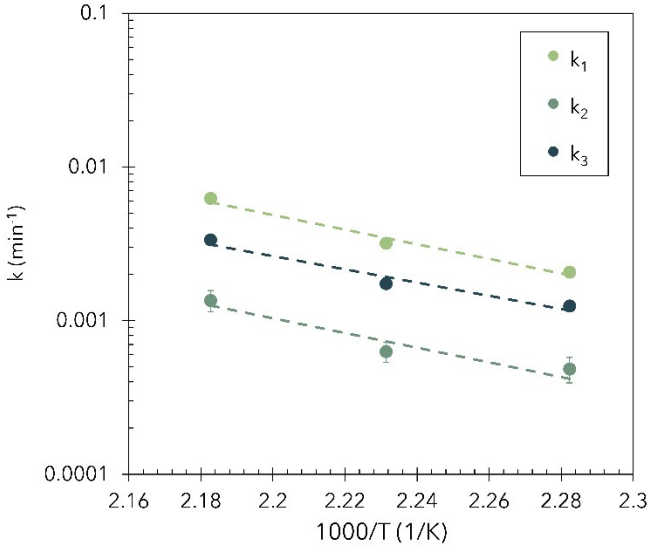


Figure S25: Arrhenius plots for the kinetic model & fits shown in Figure 4, Figure S25.

Table S3: Tabulated kinetic parameters for 3-parameter kinetic model of M-PUF acidolysis with GA*†

T (°C)	k_1 (min^{-1})	k_2 (min^{-1})	k_3 (min^{-1})
165	2.1E-03 ± 1.1E-04	4.9E-04 ± 2.7E-05	1.2E-03 ± 9.1E-05
175	3.2E-03 ± 1.3E-04	6.3E-04 ± 2.2E-05	1.7E-03 ± 9.4E-05
185	6.2E-03 ± 3.1E-04	1.4E-03 ± 4.7E-05	3.4E-03 ± 2.2E-04
E_a (kJ/mol)	91 ± 14	91 ± 28	82 ± 18
lnA	19 ± 4	17 ± 8	16 ± 5

*Values correspond to kinetic model shown in Figure 4.

†Error values for rate constants represent 95% confidence intervals; error values for E_a and lnA represent standard errors.

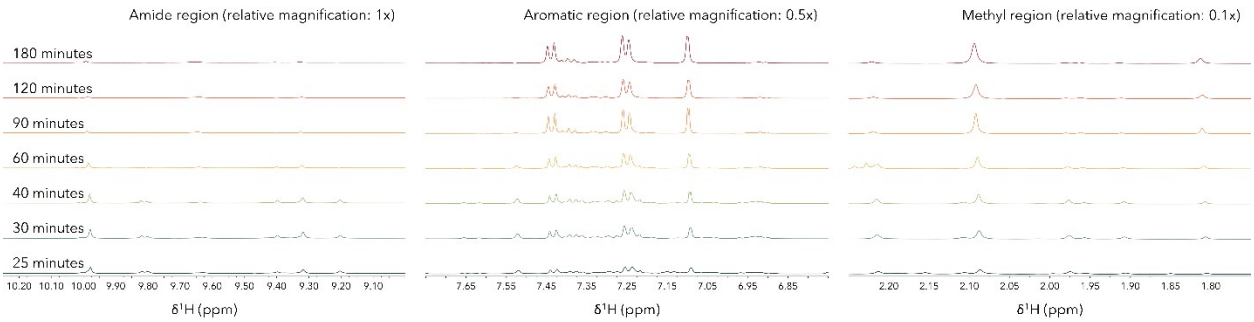


Figure S26: ^{1}H NMR of M-PUF acidolysis with SA at 165 °C and increasing reaction times. Reaction conditions: 0.5 g M-PUF, 1.5 g SA, 165 °C, 25 minutes – 3 hours under an inert (N_2) atmosphere. NMR samples: 150 mg products, 25 mg MA (internal standard), 600 µL DMSO-d_6.

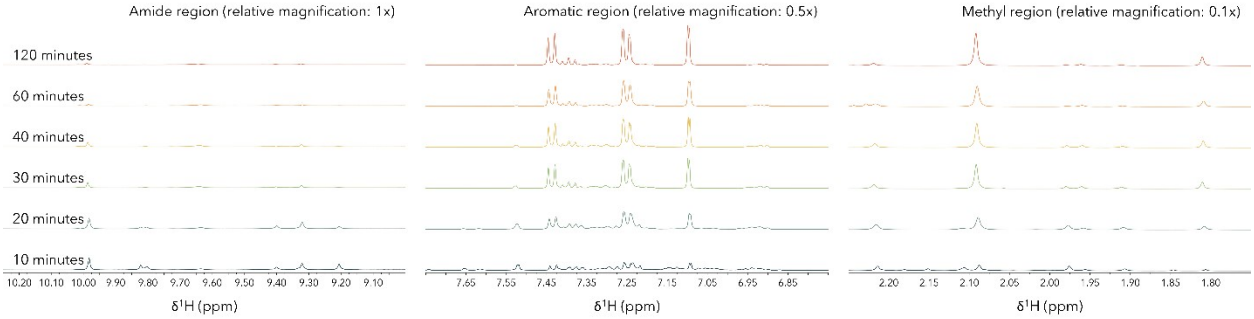


Figure S27: ^{1}H NMR of M-PUF acidolysis with SA at 175 °C and increasing reaction times. Reaction conditions: 0.5 g M-PUF, 1.5 g SA, 175 °C, 10 minutes – 2 hours under an inert (N_2) atmosphere. NMR samples: 150 mg products, 25 mg MA (internal standard), 600 µL DMSO-d_6.

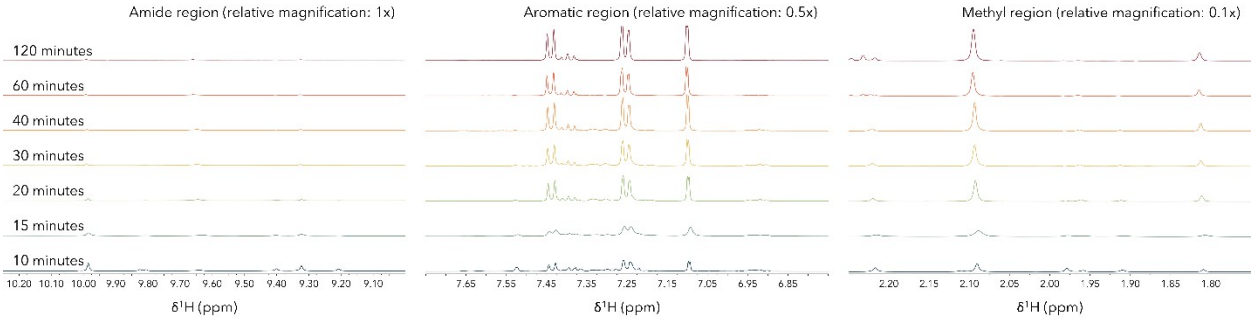


Figure S28: ^{1}H NMR of M-PUF acidolysis with SA at 185 °C and increasing reaction times. Reaction conditions: 0.5 g M-PUF, 1.5 g SA, 185 °C, 10 minutes – 2 hours under an inert (N_2) atmosphere. NMR samples: 150 mg products, 25 mg MA (internal standard), 600 µL DMSO-d_6.

Table S4: Tabulated kinetic parameters for kinetic model of M-PUF acidolysis with SA*†

T (°C)	k_1	k_2
165	0.014 ± 0.001	0.019 ± 0.003
175	0.050 ± 0.002	0.067 ± 0.011
185	0.062 ± 0.002	0.053 ± 0.006
E_a (kJ/mol)	112 ± 57	74 ± 76
lnA	26.7 ± 15.3	16.6 ± 20.3

*Values correspond to kinetic model shown in figure 5.

†Error values for rate constants represent 95% confidence intervals; error values for E_a and lnA represent standard errors.

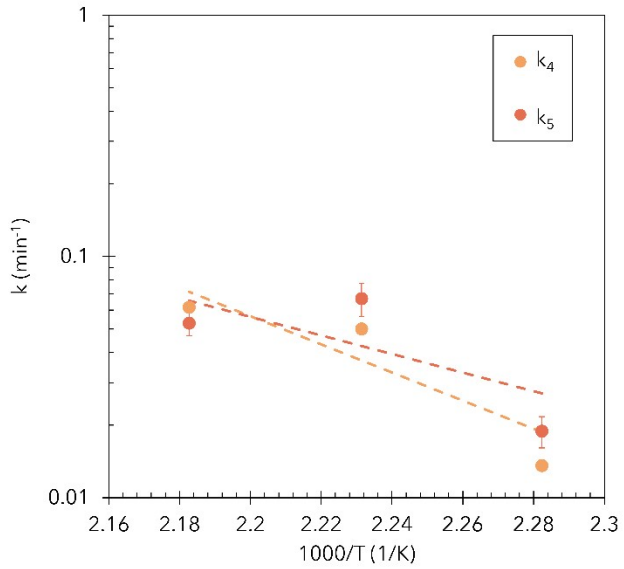


Figure S29: Arrhenius plots for the kinetic model and fits shown in Figure 5.

References

(1) William E. Acree, J., James S. Chickos. "Phase Change Data". In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, P.J. Linstrom, W. G. M. Ed.; National Institute of Standards and Technology, 2024.
(2) Westman, Z.; Liu, B.; Richardson, K.; Davis, M.; Lim, D.; Stottlemyer, A. L.; Letko, C. S.; Hooshyar, N.; Vlcek, V.; Christopher, P.; Abu-Omar, M. M. Influence of carboxylic acid structure on the kinetics of polyurethane foam acidolysis to recycled polyol. *Manuscript submitted*.