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Mechanistic Insights on the Chemical Recycling of Polyurethane Foam using Computational
and Kinetic Modeling

A dissertation submitted in partial satisfaction of the
requirements for the degree Doctor of Philosophy
in Chemical Engineering

by

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Mechanistic Insights on the Chemical Recycling of Polyurethane Foam using Computational
and Kinetic Modeling

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by

Kelsey Jean Richardson

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 6. Z. Westman, M. Perikala, X. Wu, **K. Richardson**, C. Letko, V. Vlcek, P. Christopher, M. M. Abu-Omar. Polyurethane foam acidolysis with carboxylic acids: acid structure dictates N-containing product distribution and kinetics. *Polymer Chemistry*. 2024, 15, 46, 4741-4752.
 7. Z. Westman, B. Liu, **K. Richardson**, M. Davis, D. Lim, A. Stottlemeyer, C. Letko, N. Hooshyar, V. Vlcek, P. Christopher, M. M. Abu-Omar. Influence of Carboxylic Acid Structure on the Kinetics of Polyurethane Foam Acidolysis to Recycled Polyol. *JACS Au*. 2024, 4, 8, 3194-3204.
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10. B. Liu, Z. Westman, **K. Richardson**, D. Lim, A. Stottlemeyer, T. Farmer, P. Gillis, V. Vlcek, P. Christopher, M. M. Abu-Omar. Opportunities in Closed Loop Molecular Recycling of End-of-Life Polyurethane. *ACS Sustainable Chem. Eng.* 2023, 11, 16, 6114–6128.

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ABSTRACT

Mechanistic Insights on the Chemical Recycling of Polyurethane Foam using Computational and Kinetic Modeling

by

Kelsey Jean Richardson

Polyurethane (PU) is the sixth most produced plastic globally, with 21 million metric tons produced in 2021. Its properties can be tuned by varying the structure and ratio of the polyol and isocyanate monomers used during synthesis, enabling broad use across industrial and consumer applications. As a highly crosslinked polymer with high chemical and thermal stability, conventional mechanical recycling of PU typically yields low-value products. As a result, about 80% of PU is landfilled or incinerated. Chemical recycling offers a more sustainable end-of-life pathway by recovering high-value starting materials that can be reused in PU production.

Among the available chemical recycling routes, acidolysis and glycolysis show promise due to their relatively mild reaction conditions and high-purity product streams. However, limited kinetic and mechanistic understanding has hindered their broader implementation. In this work, I combine computational chemistry and kinetic modeling to identify the molecular origins of reactivity drivers in PU acidolysis and glycolysis.

Using benzoic acid and its electronic analogues, I show that acid electrophilicity strongly influences urea acidolysis rates. I then quantify the conformational landscape of dicarboxylic acid conformations and show that acid structure and chain length govern urethane acidolysis primarily through entropic effects. In contrast, carboxyl group number affects the enthalpic barrier, as dicarboxylic acids access transition state stabilization through hydrogen bonding involving the second acid group. Finally, I present an initial study of PU glycolysis, showing how glycol polarity influences both intrinsic reactivity and apparent reactivity through mass transport effects.

Overall, this work establishes a mechanistic framework linking molecular-scale reactivity to macroscopic depolymerization behavior in PU acidolysis and glycolysis. These insights provide a foundational understanding necessary for the design of scalable PU chemical recycling processes.

TABLE OF CONTENTS

1. Introduction.....	1
1.1. Background.....	1
1.1.1. Acidolysis	4
1.1.2. Glycolysis	6
1.1.3. Other Chemical Recycling Methods	7
1.2. Research Questions	8
1.3. Overview	9
2. Methods.....	12
2.1. General DFT Principles	12
2.2. DFT in Practice	15
2.2.1. What can you calculate?	15
2.2.2. Selection of computational parameters and model system	18
2.2.3. Extension of DFT towards AIMD	20
2.3. Limitations of DFT	21
3. Differentiating Urethane and Urea Bond Activation in Polyurethane Foam	
Acidolysis	24
3.1. Introduction.....	24
3.2. Results and Discussion	26

3.2.1.	Model System	26
3.2.2.	Biphasic Kinetic Regimes of Acidolysis with MCAs.....	29
3.2.3.	Conformational and Electronic Effects on Urethane and Urea Acidolysis	35
3.3.	Conclusions.....	39
4.	Assessing the Conformational Landscape of Dicarboxylic Acids Using Ab	
	Initio Molecular Dynamics: The Role of Phase and Intermolecular Interactions.....	42
4.1.	Introduction.....	42
4.2.	Computational methods	45
4.3.	Results and discussion	49
4.3.1.	Unsaturated acids	49
4.3.2.	Saturated acids	54
4.3.3.	Connections to experimental trends.....	58
4.4.	Conclusions.....	59
5.	Mechanistic Origins of Structure-Reactivity Effects in Polyurethane	
	Acidolysis	61
5.1.	Main Text.....	61
6.	Glycol-Dependent Kinetics of Uncatalyzed Polyurethane Glycolysis	72
6.1.	Introduction.....	72
6.2.	Methods.....	74
6.2.1.	Computational.....	74
6.2.2.	Experimental	74

6.2.3.	Kinetic fitting	77
6.3.	Results and Discussion	78
6.3.1.	Reactivity results.....	78
6.3.2.	Computational results	80
6.4.	Conclusions and future work	82
7.	Other Studies	85
7.1.	Acid-Anhydride Equilibrium	85
7.2.	Carbamate to CO ₂	88
7.3.	Glycol-PUF Contact Angle Measurements	90
7.4.	PUF Morphology	93
8.	Conclusions.....	96
8.1.	Summary	96
8.2.	Outlook	99
8.2.1.	Improvements to modeling techniques	99
8.2.2.	Application of workflow to new systems	100
A.	Supporting Information for Differentiating Urethane and Urea Bond	
	Activation in Polyurethane Foam Acidolysis	102
	Materials	102
	Grinding Pre-treatment of Model PUF	103
	PUF Acidolysis Kinetic Measurement Set-Up	103

¹ H Nuclear Magnetic Resonance	107
Gel Permeation Chromatography	114
Gas Evolution.....	116
Gas Evolution Fitting.....	120
3-NBA discussion	122
Computational Analysis.....	123
 B. Supporting Information for Assessing the Conformational Landscape of Dicarboxylic Acids Using Ab Initio Molecular Dynamics: The Role of Phase and Intermolecular Interactions	 128
Computational Methods.....	128
Methods.....	128
Proton hopping in AIMD simulations.....	135
Thermostat variations.....	136
Representative Conformers.....	137
 C. Supporting Information for Mechanistic Origins of Structure-Reactivity Effects in Polyurethane Acidolysis	 139
Transition state generation workflow	139
Dicarboxylic acid chain length	142
Monocarboxylic acids vs dicarboxylic acids	145
 D. Supporting Information for Glycol-dependent kinetics of uncatalyzed polyurethane glycolysis.....	 147

Experimental Methods	147
Kinetic Fitting	151
Computational Methods.....	152
References.....	155

1. Introduction

1.1. Background

Global plastic production currently exceeds 300 million tons every year and is expected to nearly quadruple by 2050.¹ This increase in production, largely driven by an increase in population and quality of living, is predicted to account for 20% of the global oil consumption and will be associated with significant greenhouse gas emissions.¹ Plastics are an integral part of our society today, comprising a vast majority of single-use items (e.g. cups, bottles, bags, packaging, medical supplies) and consumer products (e.g. clothing, furniture, mattresses). Thus, to reduce our reliance on fossil fuel resources in plastic production, we must explore methods to increase the circularity of plastic materials.

Currently, mechanical recycling is the only large-scale alternative disposal technology for plastic waste.² Mechanical recycling involves shredding, melting, or remolding the polymer for use in a new material while maintaining its molecular structure. Although mechanical recycling rates are slowly increasing, this method is not without its limitations.³ Mechanical recycling produces lower-value products, and only certain polymers that satisfy process criteria (such as melting temperature) can even be mechanically reprocessed.² As such, an alternative disposal method that maintains the polymer utility and value is desired.

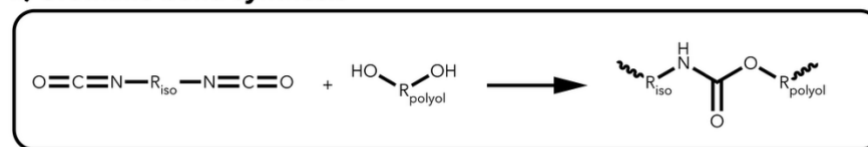
In chemical recycling, a chemical cleaving agent is used to break the polymer molecular structure into high-value small molecules and molecular building blocks, enabling the production of new polymers with desirable material properties. Unlike mechanical recycling, this method can theoretically be applied an infinite number of times, maintaining the identity,

efficacy, and value of the polymer with each iteration. This method offers great potential for achieving circularity in the plastics industry.

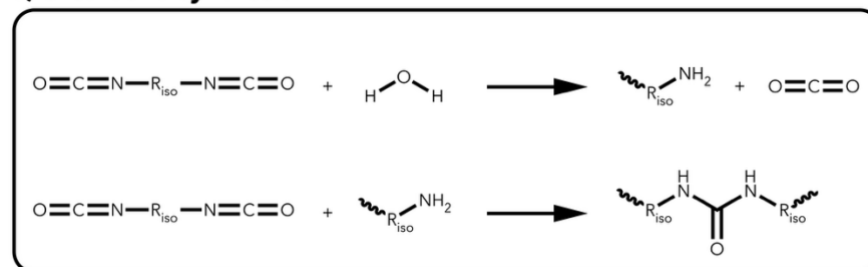
Polyurethane (PU) is the sixth most produced polymer worldwide with 21 million metric tons produced in 2021.⁴ In 2024, the PU market was around 75 billion USD and is expected to continue to grow with an annual rate of 8%.⁵ Much of the growth of the PU market is driven by the increased standards of living across the world, as PU is frequently used in construction applications for its durable and insulating properties. Depending on their chemical, thermal, and mechanical properties, PU materials can be classified as a rigid foam, flexible foam, or coating, adhesive, sealant, and elastomer (CASE). The largest volume classification of PU is flexible foam.⁶

PU foam (PUF) is synthesized through the condensation polymerization of polyol, isocyanate, and water. PUF materials contain both urethane and urea bonds. Urethane bonds are formed through the reaction of polyol and isocyanate, which arrange into soft domains (**Scheme 1.1(a)**). To form urea bonds, isocyanate groups first react with water, forming an amine and CO₂, which has the additional effect of forming bubbles in the reaction mixture and leading to the cellular structure. The amine then reacts with an additional isocyanate group to make a urea bond which assembles into a highly hydrogen bonded hard domain (**Scheme 1.1(b)**). Other components, such as catalysts, surfactants, and chain extenders are also frequently added to this reaction but will not be discussed in detail. By changing the identity of the polyol and isocyanate used, as well as their relative amounts, the resulting properties of the PUF can be tuned.⁷

a) Urethane bond synthesis



b) Urea bond synthesis



Scheme 1.1. Synthesis of urethane bonds (a) and urea bonds (b) in polyurethane polymerization.

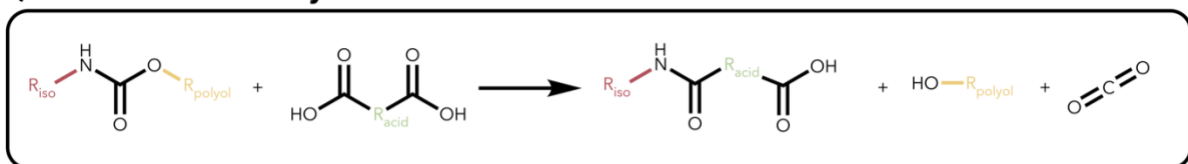
The same properties that make PU very valuable in household and industrial applications, namely its great mechanical strength and high chemical resistance, pose challenges for its disposal. Currently, approximately 80% of PU is either landfilled or incinerated. Of the recovered PU waste, a majority undergoes mechanical recycling processes such as grinding or rebinding to produce lower-value products like composites or fillers.

PU is an attractive candidate for chemical recycling due to the presence of heteroatoms (oxygen and nitrogen), making its depolymerization more facile than that of hydrocarbons. In chemical recycling, a chemical reagent (e.g., glycol, acid, water, etc.) is used to break down PU into its starting materials, polyol or isocyanate, which can then be reused in the production of new materials. Although several methods for PU chemical recycling exist, few methods have been thoroughly explored and even fewer have been implemented beyond the laboratory scale. Among these methods, glycolysis and acidolysis are the most feasible for polyurethane chemical recycling. But, we need to understand the mechanism and kinetics of the chemical recycling reactions before scale-up of these chemistries is possible.

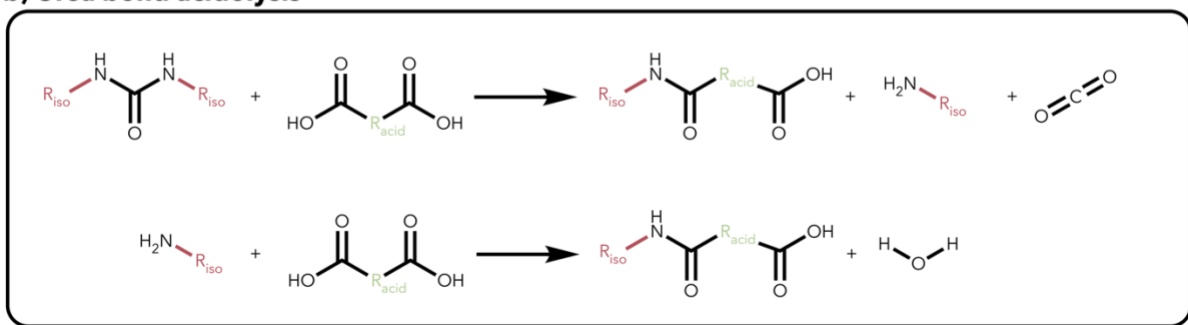
1.1.1. Acidolysis

As shown in **Scheme 1.2**, acidolysis is the reaction of PU with a carboxylic acid to form polyol, CO₂, water, and amide products. The qualitative effects of catalysts and reaction conditions on the acidolysis of PUF have been explored, but up until recent work from my group, there was a complete lack of quantitative kinetic information about this reaction.

a) Urethane bond acidolysis



b) Urea bond acidolysis



Scheme 1.2. Reaction of urethane bonds (a) and urea bonds (b) with carboxylic acid reagent in acidolysis.

Acidolysis is one of the most studied and developed recycling methods, with pilot plants such as those developed by H&S Anlagentechnik in Germany.⁸ Traditionally, laboratory studies of PU acidolysis involve a combination of high reaction temperatures (~ 200°C), long reaction times (> 4 hrs), catalysts, or alternative heating methods. For example, He et al. studied the effects of metal zinc catalysts on PU acidolysis with succinic acid (SA).⁹ They found that zinc acetate was the most efficient catalyst for this reaction, resulting in a recycled polyol with the lowest viscosity and acid value (AV) and highest hydroxyl value (OH_{number}). Gama et al. studied uncatalyzed PU acidolysis with SA at 195°C for 5 hrs, also monitoring the

AV and OH_{number} throughout the reaction.¹⁰ And finally, Gradadolnik et al. employed microwave heating at temperatures above 200°C for acidolysis with adipic acid (AA).¹¹ They utilized molecular weight as well as carboxyl, amine, and TDA content in the recycled polyol samples to probe the reaction extent.

A shared characteristic of the above studies is the absence of distinct and specific reactivity information (e.g. rate constants, reaction barriers, rate-limiting step analyses). Bulk measurements, such as viscosity and acid number, can convolve multiple phenomena, including mass transport, acidolysis, and side reactions. As a result, these measurements limit the potential learnings of these studies towards the inherent reactivity of urethane and urea groups in PU acidolysis.

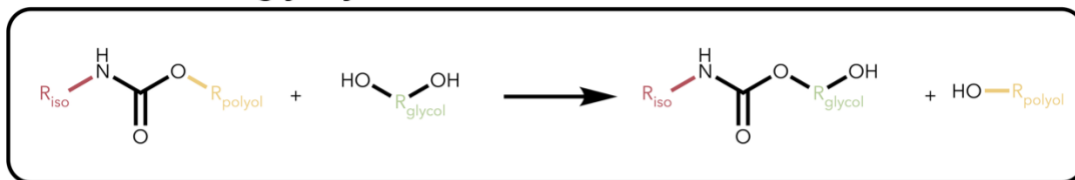
Previous work from my group found that methods to speed up PU acidolysis (catalysts, high reaction temperatures, microwave heating, etc.) were unnecessary; we discovered that this reaction could proceed in as little as 15 min at 175°C.¹² Moreover, we designed an experimental setup that allowed for observation of CO₂ evolution with 1 s resolution and verified that this gas production is concomitant with polyol release.¹³ From this kinetic analysis, we observed that the acidolysis rate constant trends with the distance between carboxyl groups in dicarboxylic acids (DCAs). However, this experimental study could not explain the mechanistic origin of this relationship.

In summary, acidolysis is well developed from a process perspective, but lacking fundamental mechanistic understandings to explain reactivity behavior, such as identification of the rate limiting step(s) and the influence of structural and energetic variations in the acid reagents on rates.

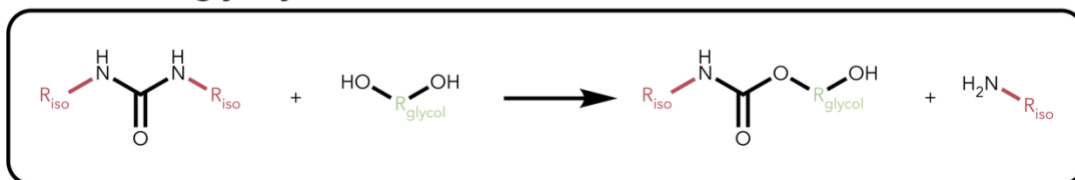
1.1.2. Glycolysis

In glycolysis, PU is depolymerized with a glycol reagent to form polyol, carbamate, and amine products (**Scheme 1.3**). This is the most developed chemical recycling method for PU, studied extensively in both academic and industrial settings, including at the pilot scale.¹⁴

a) Urethane bond glycolysis



b) Urea bond glycolysis



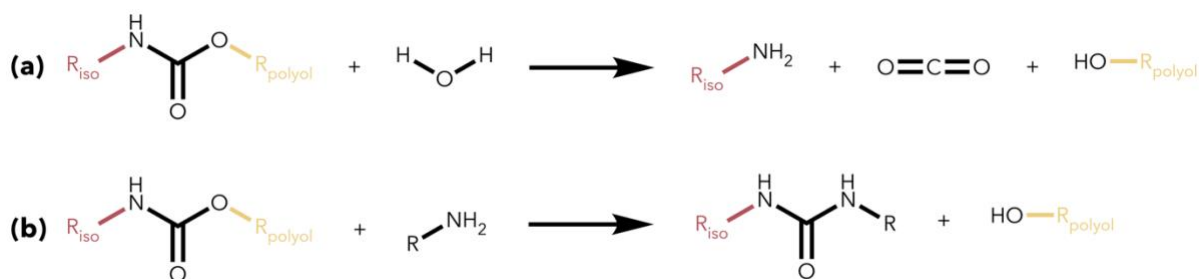
Scheme 1.3. Reaction of urethane bonds (a) and urea bonds (b) with glycol reagent in glycolysis.

Since this reaction is known to be an equilibrium process, glycols are usually added in large excess. This also can cause the reaction mixture to phase separate into a glycol-rich lower phase and polyol-rich upper phase.^{15–17} While this can be attractive as it reduces the complexity of separation steps, the heterogeneous nature of the reaction environment is an additional complication that must be considered when probing the reactivity or product distribution (e.g. taking reaction aliquots). Similar to acidolysis, catalysts, such as alkali metal hydroxides or organic metal salts, are frequently employed to enhance the reactivity.^{16,18–21} Although these studies are numerous, there is a complete lack of kinetic information (e.g. rate constants, barriers, mechanisms), for either catalyzed or uncatalyzed PU glycolysis.

In summary, although many studies have reported on novel catalysts or reaction conditions for PU glycolysis, the kinetic and mechanistic implications of changing these conditions are not well understood.

1.1.3. Other Chemical Recycling Methods

Other chemical recycling methods for PU, such as hydrolysis and aminolysis, remain underdeveloped and understudied. This is due in large part to significant disadvantages associated with these reactions, as outlined below.



Scheme 1.4. Hydrolysis (a) and aminolysis (b) of urethane bonds.

1.1.3.1. Hydrolysis

Hydrolysis is the reaction of PU with water to form amine, CO₂, and polyol products (**Scheme 1.4(a)**). Hydrolysis was one of the earliest developed PU chemical recycling methods.^{14,22} However, due to the durable and resistant nature of PU, efficient depolymerization requires the use of pressurized liquid water or high-temperature steam (200-450°C), significantly increasing the energy demand of this process.²³

1.1.3.2. Aminolysis

Aminolysis is the reaction of PU with an amine to produce urea and polyol products (**Scheme 1.4(b)**). Many different classes of aminolysis reagents have been tested, such as aliphatic and aromatic monoamines, polyamines, and ammonia. Aminolysis of PU can occur

at mild temperatures (80-190°C), but it generates a complex mixture of polyol, urea, urethane fragments, amines, and other components that necessitates difficult and expensive separations processes. Since amines are more reactive with isocyanates than hydroxyls are, the presence of amines in the reaction mixture is undesirable for the reuse of the polyol.²³

1.2. Research Questions

With the mildest operating conditions and highest value product streams, acidolysis and glycolysis are the most promising PU chemical recycling methods. However, remaining mechanistic and kinetic uncertainties limit the scale-up of these reactions. Computational modeling studies are well suited to probe the atomistic length scales associated with these outstanding questions (discussed further in **Chapter 2**). This section will overview the remaining knowledge gaps in PU recycling with acidolysis and glycolysis, suggesting how computational tools can be used to bridge these gaps, while also acknowledging the difficulties with these studies.

Firstly, there is a lack of rate constants and barriers for the acidolysis and glycolysis of PU. These kinetic parameters are necessary for any level of industrial modeling and implementation. Computational studies coupled with kinetic modeling of experimental data can be used to probe the inherent reactivities of these reactions and determine how changing the reaction environment affects depolymerization kinetics. Secondly, it has been reported by our group and others that changing the cleavage agent can strongly impact the reaction behavior (e.g. rates, product distribution, mass transport considerations), but the origin of this behavior is unclear. We can use computational studies to develop reactivity relationships while varying the reagent. And finally, the energetics of PU depolymerization vs unwanted side

reactions have not been elucidated. Computational studies can provide insight into the energetic barriers and mechanisms of the primary and side reactions.

While computational tools are well posed to interrogate these knowledge gaps, the complexities of PU chemical recycling make it difficult to model properly. Instead of simulating an entire highly complex and crosslinked “polyurethane molecule”, we must choose a model that is large enough to properly represent the system while small enough to be amenable for the modeling methods. Additionally, PU chemolysis can occur with the cleaving reagent in many different phases (solid, liquid, vapor). Proper treatment of the reagent, through the addition of solvation to computational calculations or the inclusion of intermolecular interactions in conformational considerations, is necessary to best represent experimental systems. Moreover, PU contains both urethane and urea domains; how these domains are spatially arranged and what interactions occur within and between these domains remains unclear but important in reaction modeling. As discussed in this dissertation, carefully constructed and experimentally constrained computational studies can provide mechanistic insights grounded in realistic conditions, offering a powerful methodology for interrogating PU chemical recycling.

1.3. Overview

Using computational modeling, this dissertation establishes a mechanistic foundation for understanding reactivity in PU chemical recycling. Specifically, it identifies electrophilicity, chain length, and carboxyl group number as key drivers of PU acidolysis, and glycol polarity as a governing factor in glycolysis. By integrating computational analysis with experimental observations, this work interrogates how intrinsic reactivity, conformational effects, and transport phenomena collectively influence PU depolymerization behavior.

To probe the effects of acid electrophilicity, **Chapter 3** identifies biphasic reaction kinetics in PU acidolysis with monocarboxylic acids (MCAs). Combined kinetic and computational analyses demonstrate that urea bonds are stabilized and their cleavage is accelerated by more electron withdrawing acids. Subsequent studies focus on DCAs, which contain more rotatable bonds than the MCAs previously examined. **Chapter 4** quantifies the conformational landscape of three DCAs under reaction conditions using ab initio molecular dynamics (AIMD). Intermolecular interactions in the condensed phase promote external hydrogen bonds and significantly influence acid conformations.

Chapter 5 extends this analysis by incorporating additional acids and explicit reactivity information, including transition states and barriers. A computational workflow is developed to rapidly generate transition state guesses for urethane and urea acidolysis across distributions of DCA and MCA conformations. These results show that urethane acidolysis is influenced by acid chain length, with longer acids paying larger entropic preorganization penalties. Comparison of MCAs and DCAs further reveals that DCAs exhibit faster reactivity due to stabilizing hydrogen bonds involving secondary acid groups which lower the enthalpic barrier as compared to MCAs that lack this secondary stabilization site.

Chapter 6 establishes a protocol for determining kinetic parameters in PU glycolysis, using ethylene glycol (EG) as a model system. A corresponding preliminary computational study indicates that glycol polarity governs urea bond glycolysis reactivity while urethane bond cleavage is unaffected. Finally, **Chapter 7** explores the effect of side reactions and transport or accessibility differences within the PU system. Contact angle measurements between glycols and the PU surface show that more polar glycols intercalate less into the surface, resulting in larger contact angles, whereas less polar glycols preferentially interact with the PU

and exhibit smaller contact angles. Additionally, a PU network is visualized using a graph representation to illustrate how the spatial arrangement of urethane and urea bonds may influence bond accessibility. Side reactions, influenced by reagent identity, are also examined. For example, shorter chain acids more readily form anhydrides that may influence transport behavior to the PU surface, and certain glycols are thermodynamically and sterically favored to form cyclic carbonates that may facilitate CO₂ evolution during glycolysis.

Overall, this dissertation demonstrates how computational tools, integrated with experimental observations, provide mechanistic insight into PU chemical recycling pathways that are otherwise difficult to access experimentally.

2. Methods

The following chapter outlines the principles, applications, and limitations of density functional theory (DFT), the primary computational method applied in this dissertation. The goal of this chapter is not to act as a comprehensive guide to all things DFT, but instead to give the readers a starting point from which to understand the later research and to detail some practical tips that I found especially useful along the way. There are many valuable resources that I referenced, both while writing this chapter and throughout my research. For additional and more detailed descriptions of the theoretical topics, please refer to the citations included in this chapter.

2.1. General DFT Principles

DFT is a computational method frequently used in materials science, chemistry, and engineering to predict the energetic and geometric structure of atoms and molecules.^{24–26} To do this, DFT maps the electron density of the system to a corresponding electronic structure and energy.^{27–29} While this calculation can be done exactly for systems with one electron, approximations must be made for any larger systems.

In DFT, the energy of the full interacting system is broken down into the kinetic energy of non-interacting electrons, the electrostatic interactions between non-interacting electrons, and a catch-all many-body interaction term called the exchange-correlation energy (E_{xc}).^{27,30} The exchange-correlation energy attempts to account for the error due to neglecting the energy associated with electronic interactions. While the exact functional form of this term is unknown, there are many models that express this term with differing levels of accuracy. For example, the local density approximation, the simplest approach, treats the electrons like a uniform gas, resulting in a functional that only depends on the electronic density. By

introducing additional terms, such as the derivative of the density (generalized gradient approximation (GGA) functionals) or the second derivative (meta-GGA functionals), the accuracy of this exchange-correlation term can be improved.^{31,32} Hybrid functionals include a portion of Hartree-Fock (HF) exchange energy in E_{xc} .³³ HF theory approximates electron-electron interactions as a series of single-particle interactions, offering a computationally efficient representation. While increasing the complexity of the functional usually improves its accuracy, this comes at the cost of computational time. Additionally, the behavior of different functionals in the same class can vary widely, so it is necessary to critically assess the performance of the selected functional for the desired output in any computational study.^{34,35}

An additional theoretical parameter that can be adjusted in DFT calculations is the mathematical representation of the electronic orbitals, called the basis set.³⁶ A similar principle to that applied to functionals holds – larger basis sets that can better capture the complex electronic orbitals give more accurate computational results at the expense of computational time.³⁷ Basis sets are frequently categorized based on the number of functions used in representing the valence orbitals (e.g. double zeta (DZ) refers to two independent functions per occupied valence orbital).³⁸ While selecting a basis set, the goal is to use a large enough basis to properly represent your system while maximizing the calculation efficiency.

While the functional and basis set must be specified for every DFT calculation, there are several optional parameters that can be utilized and tuned to improve the accuracy of a calculation. Firstly, dispersion corrections can be added. Many functional forms of E_{xc} do not capture long-range dispersion interactions such as hydrogen bonding.³⁹ There are several methods that attempt to address this limitation, either by adding a dispersion correction or by incorporating

non-local correlations into the functional.^{40–42} Additionally, DFT calculations are by default run in the gas phase, but solvation can influence reaction energies, charge distributions, and more. Commonly, solvation effects are added through an implicit solvent model, where the solvent is represented by a polarizable dielectric field (e.g. polarizable continuum model).⁴³ A more costly approach is to add explicit solvent molecules to clearly model how the specific solvent structure impacts the system. However, this method is typically coupled with a continuum model or molecular mechanics approaches (e.g. QM/MM or ab initio molecular dynamics).^{44–47} The inclusion of dispersion corrections or solvation methods can drastically influence the results of a DFT calculation, so it is necessary to critically evaluate when these tools should be used.

Even with these various approximations, DFT calculations often scale cubically with the number of electrons, meaning that the system size is limited by the number of electrons in the calculation.⁴⁸ For a problem like PU chemical recycling, which involves a very large and complex polymeric material, a smaller model system is used to make the calculations more tractable. When the model system and computational parameters are selected systematically and thoughtfully, computational tools are uniquely posed to yield insight into the pertinent length scales of PU chemical recycling. As shown in **Figure 2.1**, the interaction and reaction of the chemical reagents with urethane and urea moieties on the Angstrom-level scale are the relevant processes for PU chemical recycling. While shrinking core modeling (SCM) and kinetic Monte Carlo (kMC) calculations have generated insight into mm to nm PU interactions, DFT calculations of this system can yield reaction energies, reaction barriers, and relevant geometries to probe the reactive processes of interest.^{49,50}

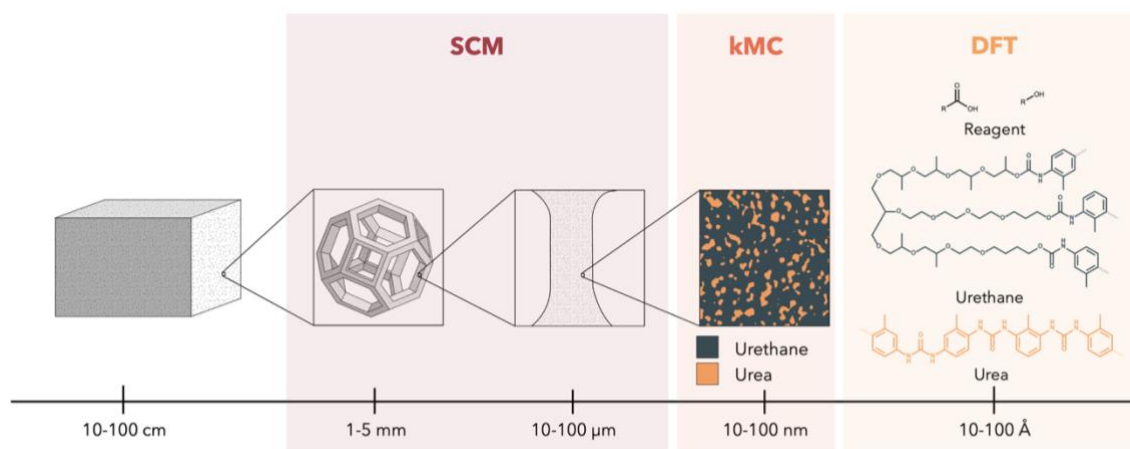


Figure 2.1. Length scales and modeling tools in polyurethane acidolysis

2.2. DFT in Practice

2.2.1. What can you calculate?

In this dissertation, there are three main categories of relevant DFT calculations: 1) local minima structures and energies, 2) transition state structures and energies, and 3) frequencies/vibrational analysis of structures of interest.

In a local minima calculation, you start with an initial guess for your geometry. From there, the DFT code calculates the energy and the gradient of the energy (forces) of the structure (using your specified exchange-correlation functional) and iteratively updates the geometry using an optimization algorithm until the forces are approximately zero. This distinguishes a local minimum on the PES. From this calculation, we have obtained information about the structure of the local minimum as well as its ground state electronic energy and translational and rotational contributions to thermochemical energies.^{51,52}

To obtain the vibrational energetic corrections, a frequency calculation is required. For this, the DFT code calculates the Hessian of the input structure (a matrix form of the second derivative of the energy) and uses a harmonic approximation to identify the vibrational

frequencies (the exact form of this approximation can vary based on the software used). At a local minimum on the PES, all of the calculated frequencies must be real numbers. These vibrational modes are used to calculate the contributions from vibrational motion to the energy, including the zero-point energy.^{53,54}

DFT can also be used to identify a transition state (TS) geometry and energy. For this, the DFT code again calculates the Hessian of the input structure and iteratively updates the geometry to move uphill in the largest vibrational mode while moving downhill along the rest, to converge upon a saddle point that contains one imaginary frequency.^{55,56} There are various methods to help with the identification of a TS, such as the nudged elastic band method or the synchronous transit-guided quasi-Newton method.⁵¹ The individual methods used to identify TSs in this dissertation will be explained in each chapter. Since the PES can be very complex, it is important to validate that the identified TS corresponds to the reaction of interest. Firstly, there should be only one imaginary frequency. Next, some visualization software (e.g. Avogadro) allows for observation of the transition associated with this imaginary mode. And finally, you can run an intrinsic reaction coordinate (IRC) calculation, that starts from the TS geometry and follows the reaction path forward or backward. The forward path should identify the pertinent reaction products while the backward path should identify the reactants.^{57,58}

From these calculations (minimum, frequency, and TS), you can determine key mechanistic information, such as the reaction energy of a process, the reaction barrier, or the activation energy. **Table 2.1** summarizes the various outputs that can be calculated with DFT, how these properties are computed, and how these are used in calculating key thermodynamic outputs.⁵⁹ It is these outputs (e.g. ΔG , $\Delta S^\ddagger$, E_a) that are used in the interrogation of PU chemical recycling methods.

Table 2.1. DFT-calculated energy terms, descriptions, and methods. RRHO = rigid rotor harmonic oscillator.

Quantity	Description	How it's computed
E_{elec}	Electronic energy at given geometry	DFT energy at geometry
F	Force at given geometry	Gradient of energy
H	Hessian; matrix of second deriv. of energy	Finite difference of gradients
Frequencies (ν_i)	Vibrational modes	From harmonic approx. of mass-weighted Hessian
Zero-point energy (ZPE)	Quantum zero-point vibrational energy	$ZPE = \sum \frac{1}{2} h\nu_i$
E_0	Electronic energy + ZPE (no thermal/entropy)	$E_0 = E_{elec} + ZPE$
$\Delta E_{thermal}(T)$	Thermal correction to internal energy at temperature T	From translational, rotational, and vibrational partition functions (RRHO/ideal-gas)
$\Delta H_{thermal}(T)$	Thermal correction to enthalpy at temperature T	From translational, rotational, and vibrational partition functions (RRHO/ideal-gas)
$S(T)$	Entropy at temperature T	From translational, rotational, and vibrational partition functions (RRHO/ideal-gas)
$H(T)$	Enthalpy at temperature T	$H(T) = E_{elec} + ZPE + \Delta H_{thermal}(T)$
$G(T)$	Gibbs free energy at temperature T	$G(T) = H(T) - TS(T)$
$\Delta X(T)$	Reaction energy for any X at temperature T	$\Delta X(T) = X_{prod}(T) - X_{react}(T)$
$\Delta X(T)^\ddagger$	Barrier for any X at temperature T	$\Delta X(T)^\ddagger = X_{TS}(T) - X_{ref}(T)$
E_a	Activation energy	$E_a = \Delta H^\ddagger + RT$

2.2.2. Selection of computational parameters and model system

To illustrate how the choice of these computational parameters affects the output observables, I calculated the activation energy (E_A) of urethane acidolysis with benzoic acid (BA) (**Fig. 2.2(a)**) using six functionals (PBE, B3LYP, wB97, PW6B95, PBE0, and HF), three basis sets (6-311G, cc-pVDZ, and cc-pVTZ), and with or without dispersion corrections (GD3BJ). As shown in **Fig. 2.2(b)**, the activation energy can change by almost 200 kJ/mol depending on the combination of computational parameters used in the DFT calculation of the reactants and transition state. Including Hartree-Fock exchange energy helps to reduce the self-interaction error, but adding too much can also lead to poor energy prediction performance. To strike this balance and to best represent experimental results, many of the calculations reported in this dissertation use PBE0 (25% exact exchange), cc-pVTZ, and dispersion corrections. Specific computational parameters will be reported in each chapter.

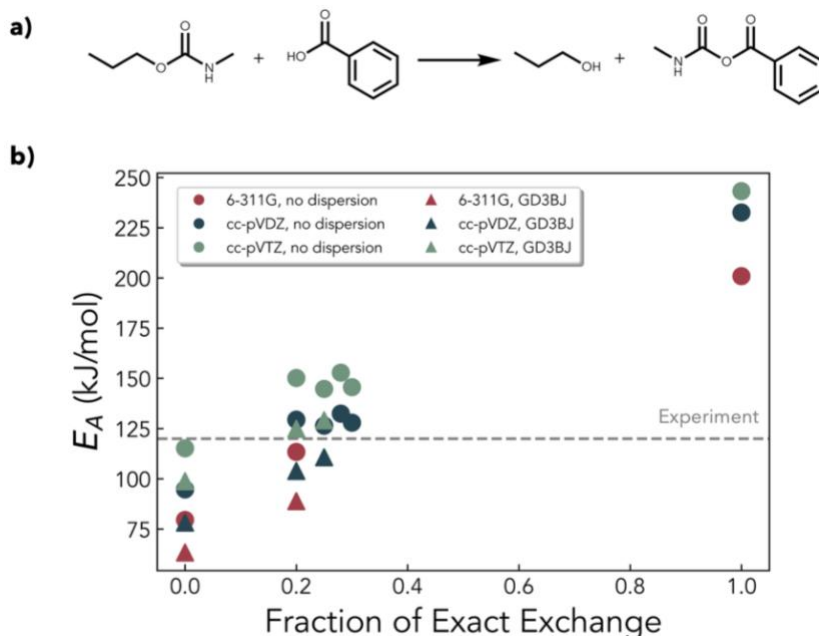


Figure 2.2. Reaction scheme of model urethane acidolysis with benzoic acid **(a)** and DFT-calculated activation energy with different computational parameters **(b)**. Dashed grey line represents experimentally determined E_A .

Another factor that influences that calculation outputs is the model system. As mentioned above, DFT calculations are done with a representative model system instead of a full polymeric system due to computational size constraints. To exemplify how the choice for this model system can impact energetics, I calculated the reaction enthalpy of urethane acidolysis with BA for model urethane of different tail lengths and branching content (**Fig. 2.3**). As the complexity of the model urethane increases, ΔH decreased accordingly. The model system used for the following calculations will be detailed in the individual chapters.

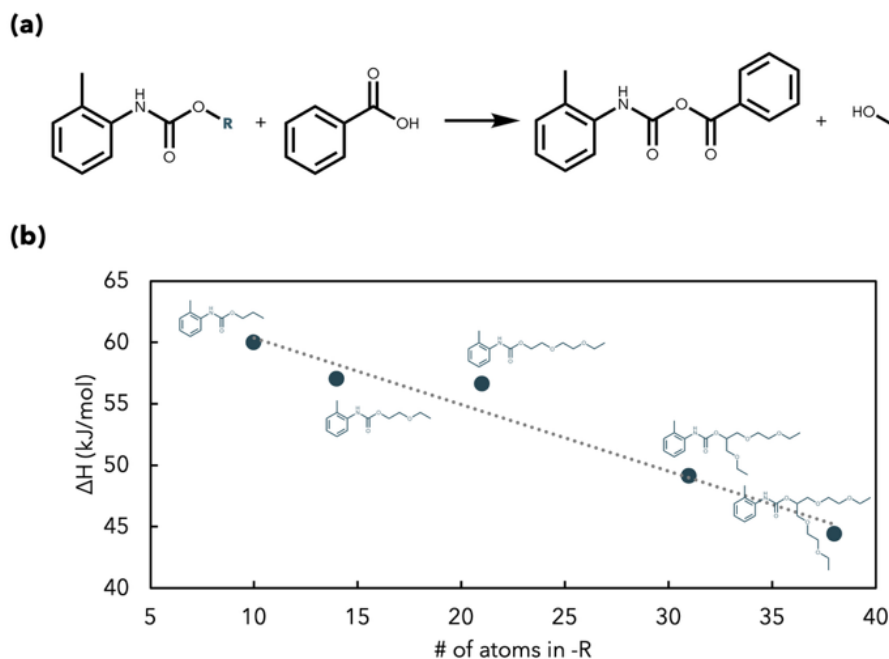


Figure 2.3. (a) General reaction scheme of urethane acidolysis with benzoic acid with polyol tail represented by R. **(b)** ΔH of urethane acidolysis reaction vs the number of atoms in the polyol tail (R). Computational details: Gaussian-16, PBE0, cc-pVTZ, butanoic acid solvent, GD3BJ.

The previous two examples highlight the importance of performing sensitivity analyses to appreciate how your system will change with both computational parameters and model system variation. While approximations are inherently included in all DFT calculations, understanding how the calculation observables can vary with these choices informs how confident you can be in conclusions.

2.2.3. Extension of DFT towards AIMD

DFT can return information (e.g. structure, energy, frequencies) about one local minimum or transition state but cannot capture energetic or structural fluctuations without running many DFT calculations at various input geometries. Ab initio molecular dynamics (AIMD) is an extension of DFT that uses forces calculated from DFT to propagate a system's geometry and energy throughout time.^{60,61} This enables for a more complete description of a system at equilibrium, including non-rare events such as thermal fluctuations and bond elongation.

Many of the theories applied in AIMD are very similar to those used in traditional molecular dynamics (MD). To start, the simulations are run in a specific ensemble with specific system constraints with respect to thermodynamic values. Commonly, the NVT ensemble is used. In this ensemble, the number of moles, volume, and temperature are held constant, matching frequently used experimental conditions. A thermostat is used to hold the average temperature constant throughout the simulation.^{62,63} A variety of thermostat methods exist, both in AIMD and MD, but all algorithms involve the addition or removal of kinetic energy from the system to maintain the simulation temperature. This can occur through stochastic collisions with an external heat bath (Anderson), the addition of a fictitious heat bath to the system energy expression (Nose-Hoover), or rescaling the system's velocity with a scaling factor (Velocity rescaling).⁶⁴⁻⁶⁶

Unlike the molecular DFT calculations described previously, AIMD calculations are run in a simulation box with periodic boundary conditions, repeating in the x, y, and z directions (DFT calculations can also be run with periodic boundary conditions). As such, the size of the simulation box can largely influence the results.^{67,68} If the box is too small, the atoms inside the simulation box can artificially interact with themselves through the periodic boundary conditions, leading to errors called finite size effects. However, if the simulation box is too large, this leads to the same computation time difficulties as having too large of a model system. It is necessary to converge the simulation outputs with respect to the box dimensions, selecting a size that is large enough to overcome finite size effects but small enough to be computationally tractable.

AIMD calculations can be split up into two regimes: equilibration and production. The production period, when the system and its resulting properties have reached equilibrium, is analyzed for output properties. Time dependent properties, such as the autocorrelation function (ACF), are monitored to determine once equilibrium has been reached.⁶⁹ This can be determined for many properties, such as velocity, temperature, or end-to-end distance. After equilibrium has been reached, the production run is analyzed to determine equilibrium properties, such as pressure, heat capacity, enthalpy, or structural information.⁶⁹ This method is applied in **Chapter 4** (which contains more implementation details) to obtain structural information about carboxylic acids used in polyurethane acidolysis.

2.3. Limitations of DFT

Approximations are inherent to the application of DFT calculations. Thus, computational tools are only as good as their inputs (computational parameters and model systems). As a

responsible practitioner of DFT, understanding the limitations and applications of this method is crucial, especially when relying upon the outputs to make scientific hypotheses and claims.⁷⁰

Many of DFT's limitations relate back to the previously discussed computational parameters. Error can be introduced through the poor choice of functional, basis set, dispersion corrections, solvation, and model systems. For one, many functionals suffer from self-interaction error or delocalization error, where an electron experiences an artificial Coulombic interaction from itself.^{71,72} Furthermore, there are specific phenomena that DFT struggles to capture accurately. For example, flexible molecules have very complicated potential energy surfaces (PESs) with many local minima. Representing the system with one finite DFT calculation may poorly capture the ensemble effect of the accessible conformations.⁷³ Additionally, entropy is very tricky to model accurately with DFT. Entropy is estimated through a rigid-rotor harmonic oscillator (RRHO) approximation based on the optimized geometry and frequencies.⁵⁹ As a result, small vibrational modes can largely influence the energy, as vibrational contributions are inversely related to the frequency. Flexible molecules may also contain low-frequency torsion that are falsely captured in the vibrational entropy analysis.

The above description of the shortcomings of DFT necessitate an explanation for when DFT is useful, especially as applied to this dissertation. It is best practice to trust DFT for relative trends within a system, but not to quantitatively match experimental results.⁷⁰ Additionally, the quantitative energetics between two distinct systems should not be compared without extreme care to ensure that systematic DFT errors that differ between the calculations are not impacting the results. In general, differences of less than 5-10 kJ/mol should be treated

with caution, relative trends are more rigorous than absolute numbers, and calculations will only be as good as their inputs.

3. Differentiating Urethane and Urea Bond Activation in Polyurethane Foam Acidolysis

This chapter is the result of a collaboration with Madeleine Davis (M.D.), Zach Westman (Z.W.), Alan L. Stottlemeyer (A.L.S), Christopher Letko (C.L.), Nasim Hooshyar (N.H.), Vojtech Vlcek (V.V.), Phillip Christopher (P.C.), and Mahdi M. Abu-Omar (M.M.A.O.). K.R., M.D., V.V., P.C., and M.M.A.O. conceptualized the work. Z.W. supervised the experimental design. M.D. conducted experiments. K.R. and M.D. analyzed the data. K.R. completed kinetic fits and computational studies. K.R. and M.D. wrote the paper. A.L.S., C.L., N.H., V.V., P.C., and M.M.A.O provided revisions. P.C. and M.M.A.O. supervised the study. Part of this chapter is published in *Chemical Science*:

Davis, M.*, Richardson, K.*, Westman, Z., Stottlemeyer, A.L., Letko, C., Hooshyar, N., Vlcek, V., Christopher, P., Abu-Omar, M. M. Differentiating Urethane and Urea Bond Activation in Polyurethane Foam Acidolysis. *Chemical Science*. **2026**, 17, 2685-2693.

*Denotes equal contribution

3.1. Introduction

Polyurethane (PU) is the sixth most used polymer globally, with a market size of 49.5 billion USD in 2023 and an annual production of approximately 26 million metric tons in 2022.^{74,75} In the synthesis of PU foams (PUF), the most common application of PU, polyols react with isocyanate groups to form urethane bonds, while added water promotes the formation of urea bonds, resulting in a polymer containing both urethane and urea linkages. The relative amount of urea and urethane linkages is tailored for desired polymer properties,

however there are constraints to ensure that PUF's desirable properties are maintained. Despite its widespread use, PU's end-of-life management remains a significant challenge. Currently, most post-consumer PUF is either landfilled or incinerated, with only 30% downcycled into lower-quality materials.⁷⁶

The limitations of mechanical recycling and environmental pressures to reduce landfilling highlight the need for efficient chemical recycling processes for PU waste.^{77–79} Chemical recycling not only reduces the environmental impact of PU disposal but also enables the recovery of high-value polyols—key components that account for the majority of a foam's mass—for use in the synthesis of new PU materials. Among known chemical recycling methods, including acidolysis, hydrolysis, aminolysis, glycolysis and other methods, acidolysis has shown particular promise for efficiently recovering high-purity polyols.^{80–85}

Previous studies have explored PU acidolysis with organic dicarboxylic acids (DCAs) and methods for polyol recovery to replace virgin polyol in new PUF products.^{86–88} However, the rate of acidolysis, particularly the interplay between urethane and urea bond depolymerization and the influence of acid electronic structure, remain poorly understood. Recent work, including our own, suggests that the structural properties of DCAs, such as the distance between acid groups, can influence PU acidolysis rates.⁸⁹ Yet, investigation into the rate of urethane versus urea bond cleavage and their dependence on acid electronics is lacking. Further, no previous studies have differentiated the rates of urea and urethane bond acidolysis, which is surprising given their chemically distinct nature.

Here, we report the rate of PU acidolysis as a function of reaction time with a set of monocarboxylic acids: benzoic acid (BA) and its electronic analogues (3-nitrobenzoic acid (3-NBA), 2-fluorobenzoic acid (2-FBA), 3-fluorobenzoic acid (3-FBA), 4-methylbenzoic acid (4-

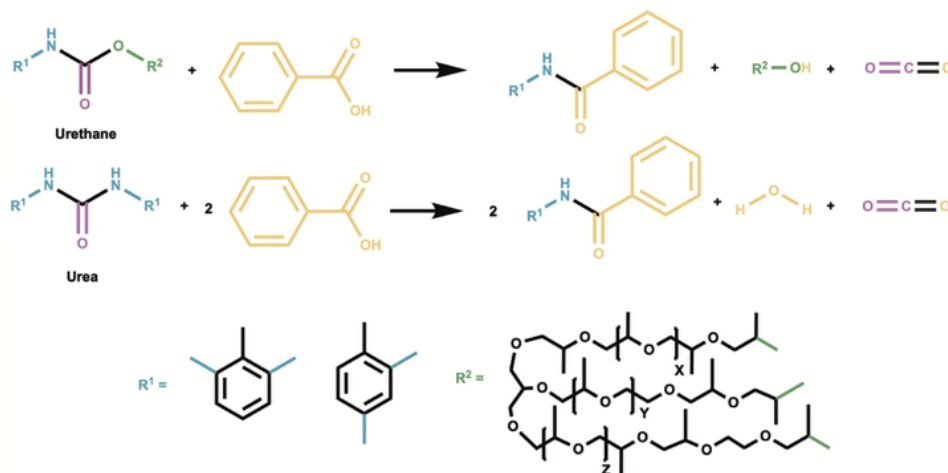
MBA), and 4-methoxybenzoic acid (4-MOBA)). Using quantitative CO₂ measurements (~1-second resolution), gel permeation chromatography (GPC), and nuclear magnetic resonance (NMR) spectroscopy, we identify biphasic kinetic behavior comprising two distinct regimes: (1) a rapid urethane bond cleavage step and (2) a slower urea bond acidolysis step. Notably, while urethane bond depolymerization rate is largely unaffected by acid electronics, the rate of urea bond scission is highly dependent on the electronic properties of BA derivatives. This is reflected in a Hammett plot with a positive reaction constant ($\rho = 3$) for urea bond acidolysis. Through computational analysis of transition states, we uncover the chemical origin of this difference, revealing distinct electronic sensitivities that govern the acidolysis of urea versus urethane bonds. We rationalize these results in the context of previous measurements of PUF acidolysis rates via DCAs and provide a mechanistic framework that accounts for the biphasic kinetic behavior in the case of BA and its derivatives, and the single-phase kinetic behavior seen with DCAs. These findings provide novel insights into the differential reactivity of urethane and urea bonds in PUFs, advancing our understanding of acidolysis mechanisms and informing the development of more effective chemical recycling strategies. Additionally, by enabling the deconvolution of urethane and urea kinetics, this information could be used to select reaction conditions that facilitate cleavage of predominantly urethane bonds, enabling rapid and efficient isolation of the high-value polyol product.

3.2. Results and Discussion

3.2.1. Model System

The model PUF (M-PUF) used in this study was synthesized by The Dow Chemical Company using toluene diisocyanate (TDI) and VORANOL™ 8136 Polyol, a heteropolymer triol typical of flexible foam formulations. The resulting M-PUF is a representative foam for

commercial applications. The reaction stoichiometry for M-PUF acidolysis with BA is shown in **Scheme 3.1**: urethane bond cleavage yields an amide, polyol, and CO₂, while urea bond scission produces an amide, CO₂, and an amine intermediate that further reacts with BA to form an additional amide and H₂O.



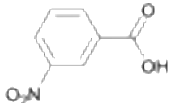
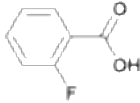
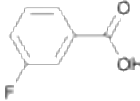
Scheme 3.1. Reaction scheme for acidolysis of urethane bonds (top) and urea bonds (bottom) with BA in model polyurethane foam (PUF). Decomposition of a urethane bond produces polyol, amide and CO₂, while decomposition of a urea bond produces amides, CO₂ and H₂O. The model foam was made using TDI (R¹) and a polyether polyol (R²).

Based on the foam formulation, the theoretical CO₂ release during acidolysis is 34 mL CO₂/g M-PUF from urea bonds and 16 mL CO₂/g M-PUF from urethane bonds (**Table A.1, A.2, A.3**). We have previously reported on the use of CO₂ evolution to measure the rate of polyurethane depolymerization with DCAs.⁸⁹ Gel permeation chromatography (GPC) and ¹H NMR spectroscopy were used to analyze the polyol (from urethane acidolysis) and amide products (from both urethane and urea acidolysis), respectively.

As shown in **Table 3.1**, we used BA and five of its derivatives (3-NBA, 2-FBA, 3-FBA, 4-MOBA, and 4-MBA) to study the influence of acid electronics on M-PUF acidolysis rates and compared the results to those from pimelic acid (PiA), a representative DCA that we

previously studied.⁸⁹ Reactions were conducted at 195°C, below the M-PUF thermal degradation temperature (> 210°C) but above the melting points of all acids.⁹⁰ A 6:1 mass ratio of acid:M-PUF (23:1 molar ratio, signifying moles of acid to total moles of urethane and urea bonds) was used to ensure efficient wetting of the foam by the acids, minimize mass transport limitations, and enable measurement of intrinsic acidolysis reaction rates.⁸⁹ The calculations for these ratios can be found in **Table A.2-A.4**.

Table 3.1. Substrate scope for kinetic study of PUF acidolysis with associated physical parameters

Acid	Hammett Constant	pKa (at 25°C)	Melting Point	Structure	Abbrev.
3-nitro benzoic acid	0.71	3.49	140 °C		3- NBA
2-fluoro benzoic acid	NA	3.27	124 °C		2-FBA
3-fluoro benzoic acid	0.34	3.87	124 °C		3-FBA
Benzoic acid	0.00	4.19	120 °C		BA
4-methyl benzoic acid	-0.17	4.37	180 °C		4-MBA
4-methoxy benzoic acid	-0.27	4.48	185 °C		4-MOBA
Pimelic acid	NA	4.48	104 °C		PiA

3.2.2. Biphasic Kinetic Regimes of Acidolysis with MCAs

Previous mechanistic and kinetic studies of PUF acidolysis have focused on DCAs, leaving MCAs largely unexplored. This is a significant knowledge gap, as MCAs may follow distinct mechanisms or reveal reactivity trends not observed with DCAs. For example, CO₂ evolution from M-PUF acidolysis with BA and PiA exhibit distinct kinetic behavior (**Figure 3.1(a)**). We note that both urea and urethane bond acidolysis stoichiometrically produce CO₂. PiA shows a single kinetic regime, consistent with prior observations for other DCAs, implying that both urea and urethane acidolysis rates can be described by a single-phase kinetic expression.⁸⁹ In contrast, BA exhibits biphasic kinetic behavior: an initial regime of faster CO₂ evolution followed by a slower regime, which has not been reported in previous studies.

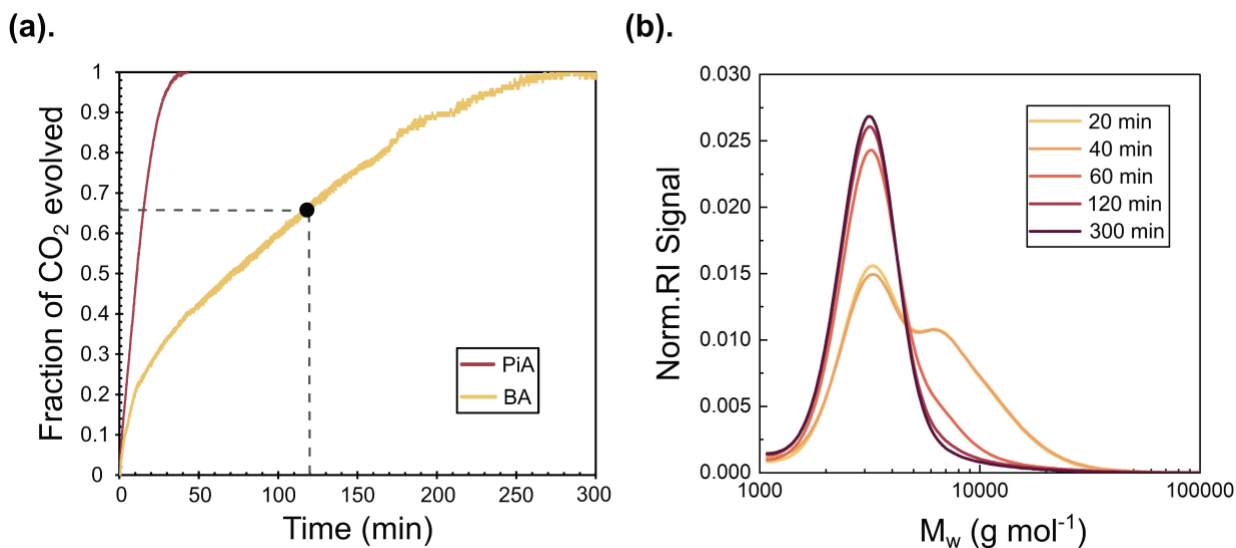


Figure 3.1. (a) CO₂ evolution (presented in fraction of total amount observed) during M-PUF acidolysis with BA and PiA. The black circle on the BA plot identifies the time when polyol release is complete, as measured by GPC. (b) Molecular weight distribution of recovered polyol from M-PUF acidolysis with benzoic acid at 195°C at varying reactions times as measured by GPC. Reaction conditions: 0.5 g M-PUF, 1.5 g PiA and 3.0 g BA, 195°C under an inert (Ar) atmosphere for both data sets.

To investigate the origin of the biphasic kinetic behavior for PUF acidolysis by BA, we monitored the reaction products using GPC and NMR. Since polyol is released exclusively through urethane bond cleavage, GPC provides a direct measure of urethane bond scission. **Figure 3.1(b)** shows GPC chromatograms of polyol released from BA acidolysis as a function of time. The main peak at 3100 g/mol corresponds to the desired monomeric polyol product (VORANOL™ 8136 Polyol), while the larger molecular weight shoulder indicates polyol oligomers. We define the completion of urethane bond acidolysis as the time at which the oligomeric tail fully disappears and the chromatogram matches that of the virgin polyol (**Figure A.11**). Based on this criterion, urethane bond acidolysis with BA is complete in 120 minutes. However, at this time (black dot in **Figure 3.1(a)**), only ~65% of the expected CO₂ has been produced. This indicates that although urethane decomposition is complete, full depolymerization of the M-PUF is not yet achieved at 120 minutes (**Figure 3.1(a)**). This deviates from our previous reports for acidolysis by DCAs, including PiA, which show full CO₂ evolution at the same time as complete polyol release (**Figure A.12**).

We complemented the GPC analysis with ¹H NMR analyses of the acidolysis products. Throughout acidolysis, as polyurethane bonds are chemically cleaved, products of a variety of molecular weights and reactive end groups are produced. Due to this highly heterogeneous intermediate product mixture, the ¹H NMR spectra of reaction samples during acidolysis contains many signals of varying dispersity and overlap. As a result, ¹H NMR is most accurately applied to determine when all acidolysis is complete, since the reaction mixture will be homogeneous and of a known composition. NMR spectra were taken of reaction aliquots starting when the reaction mixture was fully solubilized and ending when gas evolution ceased. Small molecule models of urethane and urea bonds (**Figure A.2**), in addition to previous

literature reports, were used to guide the peak assignments. Amide signals ($\delta = 9.5\text{--}10.5$ ppm) and oligomeric urea signals ($\delta = 8.3\text{--}9.3$ ppm) help inform the extent of urethane and urea bond acidolysis (Figure 3.2).^{86,87,91–93} Following completion of urethane bond acidolysis (as indicated by full polyol release in the GPC at 120 minutes), the NMR spectra continue to evolve as a function of time; amide product signals increase, and oligomeric urea signals persist until 300 minutes. Beyond this time, the ^1H NMR spectra remain unchanged with only the amide signals expected from the products in this region. Figure 3.2 assigns these peaks to amide products from the 2,4 and 2,6 TDI used in the M-PUF formulation. Peak integrals can be found in Figure A.3. This NMR analysis further supports the gas evolution data (Figure 3.1(a)) which indicates that full acidolysis of both urethane and urea bonds is complete at 300 minutes.

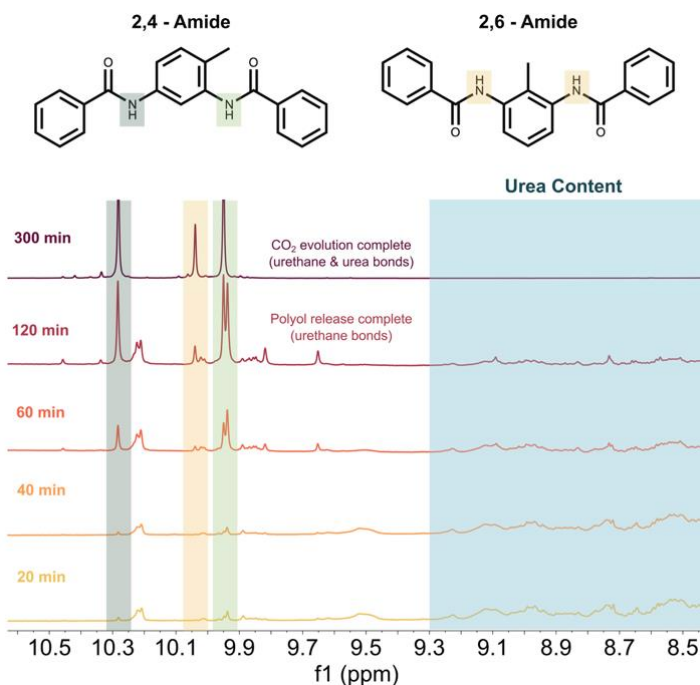


Figure 3.2. ^1H NMR spectra of reaction products from M-PUF acidolysis with BA at 195 °C at several time points (solvent: DMSO- d_6). Shaded region highlights signals assigned to oligomeric urea content. Reaction conditions: 0.5 g M-PUF, 3.0 g BA, 195 °C under an inert (Ar) atmosphere.

To test the robustness of this kinetic phenomenon, we ran additional experiments with added catalysts and different foam formulations. In the PUF synthesis process, catalysts such as Dabco T-9 and Dabco 33 LV are used and not removed. Even when adding double the amount used during PUF synthesis, the acidolysis kinetics, including the biphasic behavior, do not significantly change (**Figure A.14**). This indicates that these residual additives do not impact the monitored reaction, likely because they are too dilute. Moreover, we carried out these reactions with two additional PUF formulations of varying amounts of urethane and urea bonds as well as an end of life (EOL) PUF. Once again, we do not observe any significant change in the gas evolution kinetics, signifying that our observations and conclusions are robust to a wide range of commercially relevant foam formulations (**Figure A.15-A.16**).

These results provide strong evidence that during M-PUF acidolysis by BA, urethane bond decomposition occurs during the initial, faster kinetic regime while urea bond decomposition predominantly occurs in the slower kinetic regime. GPC analysis confirms that polyol release is complete at 120 minutes, and the amount of CO₂ evolved at this time corresponds to full stoichiometric release from urethane bonds (with a small additional amount from the onset of urea acidolysis). From 120 to 300 minutes, CO₂ continues to evolve. Since urethane decomposition is complete, this gas evolution must be due to urea bond acidolysis. Finally, ¹H NMR further confirms that acidolysis of both urethane and urea bonds is complete at this time. In summary, urethane cleavage occurs during the initial gas evolution regime while urea decomposition primarily occurs during the slower kinetic regime. These analysis methods and conclusions are outlined in **Table A.5**.

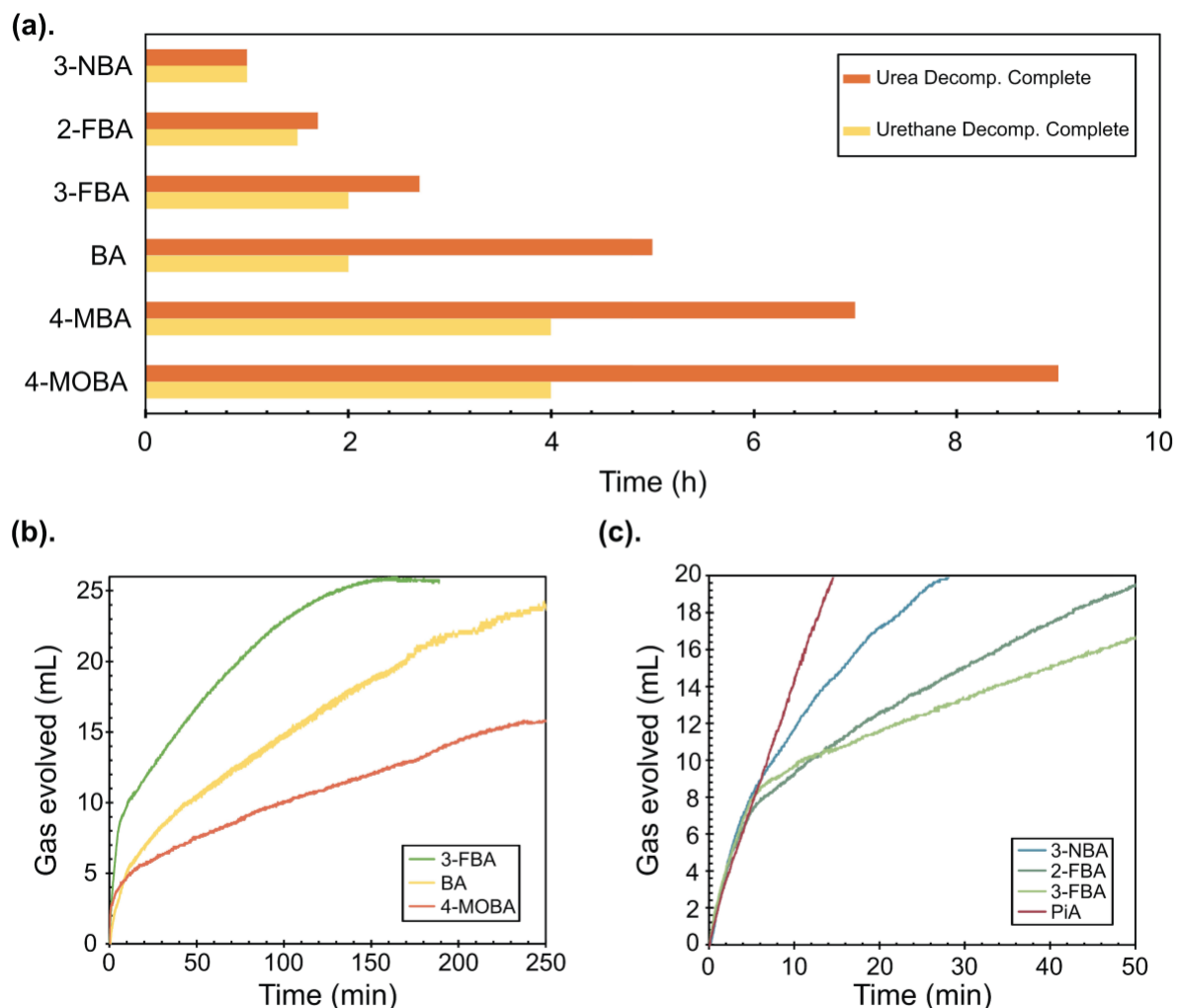


Figure 3.3. (a). Time (h) for urethane bond decomposition to complete according to GPC and for urea bond decomposition to complete according to CO₂ evolution for the studied MCAs. (b). CO₂ evolution during M-PUF acidolysis with 3-FBA, BA and 4-MOBA, showing the biphasic kinetics (c). CO₂ evolution during M-PUF acidolysis with the three fastest MCAs studied, 3-NBA, 2-FBA, 3-FBA, and PiA, zoomed in to show their initial regimes. Reaction conditions: 0.5 g M-PUF, 1.5 g PiA and 3.0 g 3-NBA/2-FBA/3-FBA, 195°C under an inert (Ar) atmosphere.

To determine whether this biphasic behavior is specific to BA or broadly applicable to MCAs, we compared the time required for urethane and urea bond decomposition across all MCAs studied, using the time of complete polyol and CO₂ release, respectively (**Figure**

3.3(a)). Due to experimental limitations with the slowest acids (4-MBA and 4-MOBA), we extrapolated the time of complete CO₂ release from the initial slow regime behavior. More information about this can be found in **Appendix A**. In all cases, except for 3-NBA which will be discussed more below, we observe polyol release consistently preceding full CO₂ evolution. Interestingly, the time required for complete decomposition of urea bonds varied significantly, from 1 h for 3-NBA to 9 h for 4-MOBA (**Figures A.5-A.9**). Conversely, the time for urethane acidolysis only slightly varies with different acids tested and does not strongly trend with the acid electronics as discussed in future sections. The CO₂ plots for these acids also displayed biphasic behavior, as seen in **Figure 3.3(b)**, with 3-FBA as a representative electron withdrawing substituted acid and 4-MOBA as an example electron donating substituted acid (see **Figure A.13** for full gas evolution plots). To our knowledge, this is the first study to resolve the distinct kinetic regimes of urethane and urea bond decomposition in PUF depolymerization.

To extend this analysis, we compared the initial rates of CO₂ release during M-PUF acidolysis, corresponding to the predominantly urethane regime, with the fastest MCAs (3-NBA, 2-FBA, and 3-FBA) to PiA, a representative DCA (**Figure 3.3(c)**). Rates of urethane bond depolymerization were comparable across all MCAs and PiA, implying that urethane bond acidolysis is largely unaffected by electronic effects. In contrast, urea bond decomposition, represented by the second regime, was consistently slower for all MCAs relative to PiA.

To understand the kinetic implications of this behavior, we can compare the results of acidolysis with MCAs to those previously obtained by our group with DCAs. We hypothesize that in all PUF acidolysis reactions, not just those reported here for MCAs, urethane groups

must be decomposed first to reveal urea linkages due to the structure of the material. Due to the polar nature of the urea linkages, these domains form strongly hydrogen bonded segments inside of softer, and more accessible, urethane domains.^{94,95} This phase-separation, in addition to the inherent reactivity differences of MCAs with urethane and urea bonds, is likely contributing to this observed behavior.

In MCA-mediated reactions, urea bond decomposition is slower than urethane bond decomposition, occurring in the second regime. Urethane bonds are cleaved rapidly, exposing less-reactive urea bonds, leading to the observed biphasic kinetics. We can contrast DCA-mediated acidolysis. We can say definitively that urea bond decomposition is no longer rate limiting, since we observe mono instead of biphasic kinetic. Instead, we hypothesize that urethane bond acidolysis is rate-limiting. Once the urea bonds are exposed, they decompose with faster intrinsic rates than urethane bonds. As a result, CO₂ from both urea and urethane bonds is released concurrently with polyol, resulting in a single kinetic regime. This mechanistic distinction emphasizes the importance of studying acidolysis with MCAs to develop a fuller understanding of bond-specific (urea vs urethane) reactivity and kinetic behavior in PUF depolymerization. This also implies that urea bond acidolysis must be particularly sensitive to the nature of the acid, as this step must be much slower for BA than previously studied DCAs for this mechanistic picture to be true.

3.2.3. Conformational and Electronic Effects on Urethane and Urea Acidolysis

As shown in **Figure 3.3(a)**, the time required for complete urethane bond acidolysis is largely independent of acid electronic structure, while that for urea bond acidolysis varies significantly with electronic substituents. To further support this observation, we fit the CO₂ evolution data to a biexponential model and used the extracted rate constants to construct a

Hammett correlation. Details of the fitting procedure are provided in **Appendix A**. Note that 2-FBA is excluded from the Hammett correlations (**Figure 3.4(b)** and **(d)**) because it is difficult to quantify a Hammett constant that captures only electronic effects, not steric effects, for an ortho substituent.⁹⁶

As hypothesized, the rates of the initial urethane regime are larger than that of the urea regime for all acids (**Figure 3.4(a)** and **(c)**). Additionally, as shown in **Figure 3.3(b)** and **(d)**, the urethane acidolysis rate is mostly independent of acid electronics, while the urea rate shows a strong dependence on acid electronics, as demonstrated by a Hammett plot with a strong positive slope ($\rho=3.00 \pm 0.01$).

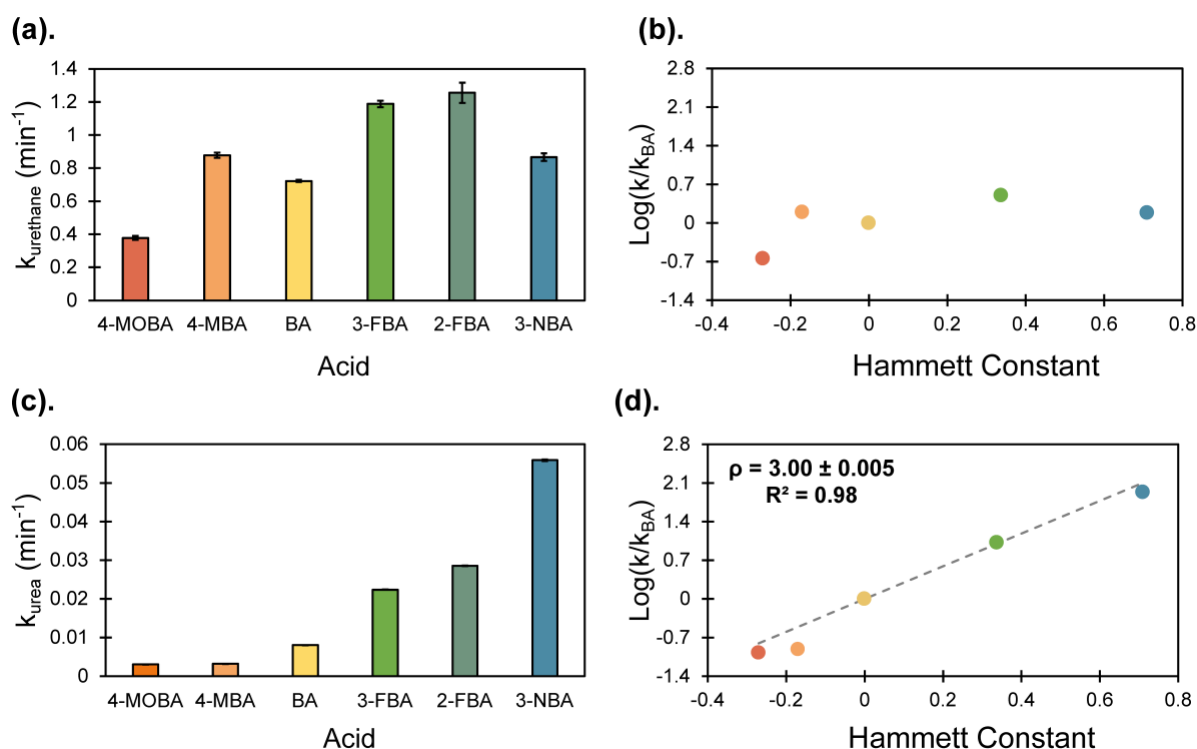


Figure 3.4. (a) Apparent first-order rate constants for the first kinetic regime (urethane bond acidolysis) derived from CO_2 evolution over time at 195°C (k_{urethane}). Error bars represent the standard error of the rate constants, accounting for variability from both experimental replicates and the fitting procedure. (b) Hammett plot for urethane acidolysis, showing the relationship between the acid Hammett constant

and the logarithm of the normalized k_{urethane} values (each acid normalized by k_{urethane} for BA). (c) Apparent first-order rate constants for the second kinetic regime (urea bond acidolysis) derived from CO_2 evolution over time at 195°C (k_{urea}). Error bars represent the standard error of the rate constants, accounting for variability from both experimental replicates and the fitting procedure. Note the different y-axis scale from (a) to better compare urea rates. (d) Hammet plot for urea acidolysis, showing the relationship between the acid Hammett constant and the logarithm of the normalized k_{urea} values (each acid normalized by k_{urea} for BA). The dashed line represents the linear fit, constrained to pass through the origin, with the slope (ρ) indicated.

Notably, 3-NBA, the most electron withdrawing acid tested, appeared to display a near single kinetic regime. However, quantitative fitting showed that a biexponential model provided a better fit than a single first order model (**Figure A.19**). We hypothesize that the electronically accelerated urea bond acidolysis rate shifts the rate-limiting step closer to urethane bond acidolysis in 3-NBA, similar to DCA acidolysis. This comparison underscores the pronounced electronic sensitivity of urea bond acidolysis, in contrast to the electronic insensitivity of urethane bond cleavage.

While here we show that urethane bond acidolysis rate is largely insensitive to acid electronic effects, we have observed previously that urethane bond decomposition is sensitive to the chain length of the DCA acidolysis reagent.^{89,97} For example, urethane bond acidolysis is accelerated with acids with fewer carbons between the two acid groups. At longer chain lengths in DCAs, such as in PiA, this cooperative effect diminishes, and the urethane rate approaches that of MCAs.

In contrast, urea bond decomposition is now observed to be sensitive to both conformational and electronic influences. Although BA and PiA have similar acid strengths ($\text{pK}_a = 4.20$ and 4.48 , respectively), urea bond decomposition is consistently slower with BA

and all MCAs than with DCAs. This suggests that the presence of only one acid group limits both the cooperative conformational and the electronic stabilization influences in urea bond acidolysis. Thus, urea bond acidolysis rates seem to be sensitive to both acid electronic and conformational effects, whereas urethane bond acidolysis is only sensitive to conformational effects observed as a function of DCA carbon chain length. The exact nature of the proposed conformational effect will be the subject of future studies.

To understand the molecular origin of this differential sensitivity to electronic effects in urea and urethane bonds, we conducted a computational analysis of the urethane and urea acidolysis reaction pathways using DFT [M06-2X/cc-pVTZ] with Gaussian-16.⁹⁸ Through this analysis, we found that the activation barriers for urethane acidolysis were largely consistent regardless of acid reagent while urea barriers varied greatly (**Figure A.21(a)** and **A.21(b)**). These barriers were used to computationally replicate the experimentally observed Hammett correlations (**Figure A.21(c)** and **A.21(d)**). Additionally, both urethane and urea bond decomposition proceed through six-centered transition states (see **Appendix A** for more details). For urea, DFT-optimized geometries show that more electron withdrawing acids yield a later, more delocalized TS, as evidenced by elongation of the C6-N5 bond by ~ 0.05 Å and the O3-H4 bond by 0.1 Å (**Figure 3.5(a)**). Consistent with these geometric trends, we propose that the acceleration in urea acidolysis rates with electron withdrawing groups can be attributed to these groups stabilizing charge in the transition state, leading to the observed geometric elongation towards a later transition state. Conversely, the urethane acidolysis transition state structure does not change with electronic substitutions, consistent with experimental observations (**Figure 3.5(c)**). We hypothesize that this is due to the inherently higher electronegativity of the urethane oxygen acceptor (atom 5, **Figure 3.5(d)**), which stabilizes the

transition state and reduces dependence on acid electronics. This provides a structural basis for the experimentally observed electronic insensitivity of urethane acidolysis and the enhanced reactivity of urea bonds, further supporting the mechanistic regimes identified in our kinetic studies.

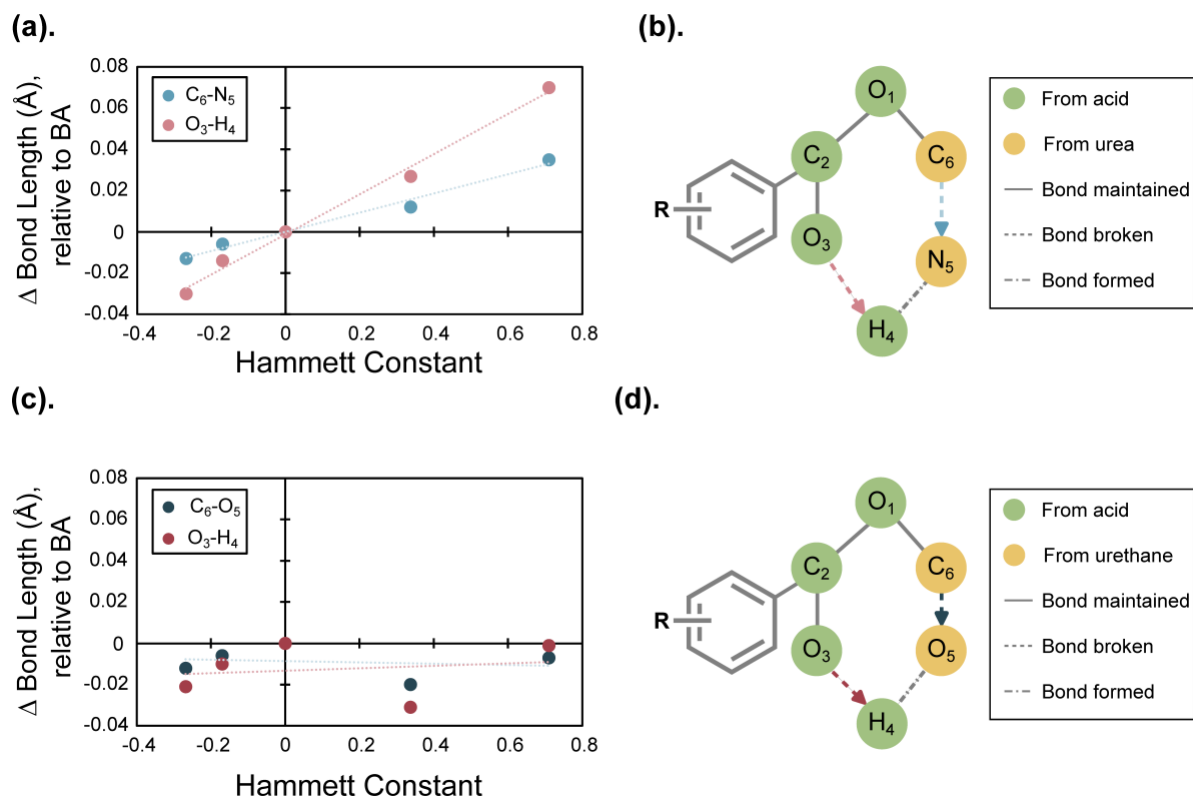


Figure 3.5. Urea acidolysis DFT-calculated bond lengths in transition state with different acids, normalized by the bond length in BA (a) and transition state structure (b). Urethane acidolysis DFT-calculated bond lengths in transition state with different acids, normalized by the bond length in BA (c) and transition state structure (d). Theory information: Gaussian-16, M06-2X, cc-pVTZ, GD3, T=448K, in vacuum.

3.3. Conclusions

This work provides new insights into the kinetics of PU depolymerization, revealing unique reactivities and stabilizing influences for urethane versus urea bond acidolysis. Through

acidolysis with BA and other MCAs, we identified biphasic kinetics and successfully deconvoluted the regimes into rapid urethane bond decomposition followed by slower urea bond cleavage.

Urethane bond acidolysis was found to be directed exclusively by conformational factors; acidolysis rates increase with proximal carboxyl groups, as seen with short-chain DCAs, and are independent of the acid electronic structure or pKa. In contrast, urea bond cleavage is influenced by both conformational and electronic influences. Electron-withdrawing acids accelerate the urea acidolysis rate, as demonstrated by a Hammett plot with $\rho=3.00 \pm 0.01$. However, even the most electron withdrawing MCAs are slower than DCAs, emphasizing the additional conformational stabilization provided by a second acid group. Transition state analyses support this distinction; electron withdrawing groups stabilize the urea transition state through charge delocalization and bond elongation, while the urethane transition state remains structurally invariant with respect to acid electronics.

We further propose that DCA- and MCA- mediated acidolysis have a different rate-limiting step. For DCAs, we only observe one kinetic regime that correlates with acid chain length, but not pKa, indicating that urethane bond acidolysis is rate-limiting and conceals any electronic variations in the urea rate. In MCA systems, urethane bond decomposition occurs rapidly, exposing the less-reactive, rate-limiting urea bonds, and giving rise to the observed biphasic kinetics.

This study provides the first molecular-level understanding of the distinct reactivity of urethane and urea bonds during PU acidolysis with carboxylic acids, linking these differences to conformational, electronic and transition state (computational) insights. These insights

deepen our understanding of PUF acidolysis mechanisms, providing valuable guidance for optimizing chemical recycling strategies for polyurethane waste.

4. Assessing the Conformational Landscape of Dicarboxylic Acids

Using Ab Initio Molecular Dynamics: The Role of Phase and

Intermolecular Interactions

This chapter is the result of a collaboration with Mahdi M. Abu-Omar (M.M.A.O.), Phillip Christopher (P.C.), Vojtech Vlcek (V.V.), K.R., M.M.A.O, P.C., and V.V. conceptualized the work. K.R. conducted computational studies, analyzed the data, and wrote the paper. M.M.A.O, P.C., and V.V. provided revisions. P.C. and V.V. supervised the study. Part of this chapter is published in The Journal of Physical Chemistry B:

Richardson, K., Abu-Omar, M.M., Christopher, P., Vlcek, V. Assessing the Conformational Landscape of Dicarboxylic Acids Using Ab Initio Molecular Dynamics: The Role of Phase and Intermolecular Interactions. *J Phys Chem B*. **2025**, 129, 28, 7195-7202.

4.1. Introduction

Molecules composed of more than just a few atoms often co-exist in distinct geometric conformations, depending on the free energies of the various conformers.^{99,100} It is well known that different molecular conformations can have distinctive reactivities.^{101–104} It has also been shown that these conformational and reactivity differences can be solvent-specific, suggesting that interactions with the environment drive changes in the free energies of molecular conformations that in turn may dictate the reactivity of the mixture.¹⁰⁵ As such, attempts to predict reactivities of molecules in solvated systems must take into account intermolecular interactions and their influence on the free energies of molecular conformations.

One of the simplest examples is the conformational landscape of dicarboxylic acids (DCAs), where at least two conformations are energetically accessible for short-chain DCAs: a ring-like conformer where the two acid groups interact and a chain-like conformer where the molecule is extended. DCAs are technologically important as they find use in a variety of chemistries and industries, such as in the synthesis of pharmaceuticals and chemical precursors.¹⁰⁶ DCAs have also been demonstrated as a viable reagent for polyurethane chemical recycling via acidolysis.^{23,107,108} A recent study found that variations in the DCA chain length causes an order of magnitude difference in acidolysis rate constants without a change in apparent activation barrier.⁸⁹ It was hypothesized that the DCAs existed in various conformations and that the difference in rate constant was controlled by the fraction of DCA existing in a particular reactive conformer. Polyurethane acidolysis can be run either with DCAs in the vapor phase or with DCAs in the liquid phase, where they serve as both the solvent and the reactant. Therefore, these observations of polyurethane acidolysis with DCAs motivate an analysis of the influence of preferred DCA conformers with influence of intermolecular interactions through simulations of conformations in both the vapor and condensed phases.

Previous reports have studied the free energy landscape of DCAs conformations in the vapor and aqueous phases using static techniques, such as density functional theory (DFT) calculations with local geometry optimization.^{109–112} However, these fixed approaches fail to take into consideration the full free energy landscape of molecules and often identify just a few local energy (geometry) minima depending on initial geometries in the calculation. Succinic acid (SA), for example, can exist in more than 100 plausible conformers based on the flexibility of carbon-carbon and carbon-oxygen bonds;¹¹³ the conformational landscape is more complex than just the two orientations of the acid groups described above. Contrastingly, benzoic acid,

a benzene ring with one carboxylic acid substituent, can only occur in four plausible conformers based on the number of rotatable bonds. Particularly for molecules with flexibility and mobility, such as end group rotation and backbone bending, molecules are constantly fluctuating and sampling a number of conformations at equilibrium.⁹⁹ Clearly, intermolecular interactions in condensed phases, which are important to understand the reactivity of DCAs, will further complicate this landscape.

In this paper we use DFT-based ab initio molecular dynamics (AIMD) to study the influence of density (varying from vapor to liquid-like density) on the conformational distribution of three DCAs with varying structure (fumaric acid (FA), maleic acid (MA), and SA, **Figure 4.1**). AIMD can sample the distribution of conformations at equilibrium, provided that the kinetics of conformational changes are sufficiently fast, and has been recently been used for simulating the condensed phases of organic systems.^{114,115} We show that DCAs with adaptable hydrogen-bonding configurations, such as MA and SA which can form internal or external hydrogen bonds, are more likely to form intermolecular interactions in response to increasing system density and thus the conformational landscape is strongly influenced by system density. Comparatively, the conformational distributions of structurally constrained DCAs, such as FA, demonstrate a weaker dependence on system density as there are fewer structural changes that can occur to promote intermolecular hydrogen bonds. Besides the fundamental insights into the behavior of DCAs, this study highlights the advantages of using AIMD for the conformational analysis of condensed systems and suggests that the density of the system could be used to modulate reactivity of aliphatic DCAs in polyurethane acidolysis and other reactions where conformations dictate reactivity.

4.2. Computational methods

In this study both vapor-phase and condensed-phase systems of FA, MA, and SA were simulated with AIMD, and the resulting molecular conformations were compared to those calculated by direct energy minimization. Both types of simulations were performed using DFT at the same level of accuracy, which is described further below. Simulations of DCAs at vapor phase concentrations with AIMD were carried out with one acid molecule in a $20 \times 20 \times 20 \text{ \AA}^3$ box to minimize any interactions between molecules, resulting in a density of approximately 0.02 g/cm^3 for all acids (**Table B.1**). For AIMD simulations of DCAs in the condensed phase, the box size was selected to ensure a density of 1.2 g/cm^3 , an estimate of the average DCA liquid phase density based on the densities of acetic and formic acids, unless otherwise noted (**Table B.1**). Observables of the simulation were converged with respect to the number of acid molecules in the simulation to ensure that there were no finite size errors in the calculations (**Fig. B.2**). The initial configuration of the conformation of molecules was found to have no effect on the final distribution, given that the system was given sufficient time to equilibrate (**Fig. B.3**). Details of the initial configurations used in this study are provided in **Fig. B.4**. Initial velocities were determined by a Boltzmann distribution at 473 K, a pertinent temperature for polyurethane acidolysis and other chemistries involving DCAs.

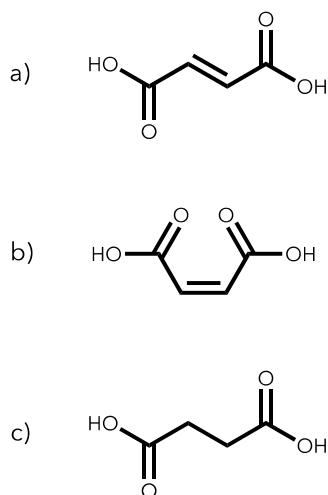


Figure 4.1. a) Fumaric acid, b) maleic acid, and c) succinic acid

AIMD simulations were performed in the canonical ensemble (constant N , V , and T) using Vienna Ab initio Simulation Package (VASP) with a planewave cutoff energy of 500 eV (**Fig. B.1**) and the PBE functional with the projector augmented wave (PAW) method.^{116–120} The simulation average temperature was held constant at 473 K using the Andersen thermostat.⁶⁵ To test the robustness of our results to other thermostats, we redid the SA condensed phase simulation with the Nose-Hoover thermostat and compared the results (see **Appendix B** for more details). The simulations had 1 fs time steps and included long-range Tkatchenko–Scheffler corrections accounting for weak non-local correlations.¹²¹ See Fig. B.9 and **B.10** for example simulation input files.

The equilibration period, where the system evolved from initial geometries to geometries that are representative of the equilibrium conformer distribution, was determined by monitoring the moment of inertia (I) autocorrelation function of the system (**Fig. B.5**). $I = \sum m_i r_i^2$, where m_i is the mass of the atoms and r_i is the distance of each atom from the center of mass. While there are many variables that can be used to monitor the geometry of molecules, such as certain bond distances and end-to-end distances, the moment of inertia accounts for the

atomic distribution of the entire molecule around the center of mass instead of comparing finite points. Additionally, I values between distinct conformers of DCAs (i.e. ring vs chain, as shown below) are distinct enough to differentiate (e.g., ~20% difference in I for ring and chain, which is larger in magnitude than the distribution of I for a single conformer). For consistency, the equilibration period was taken as 35 ps for each simulation. This was the maximum length of time required to reach equilibration for the systems studied (**Fig. B.5**).

In the production period (where characteristics of the molecules at equilibrium occur), we computed the probability of hydrogen bond formation according to the details below (**Fig. B.6** and **B.7**). The presence of internal hydrogen bonds was determined by calculating the distance between the acid group proton and carbonyl oxygen for both acid groups. If the minimum distance was less than 3.3 Å, a common cutoff in hydrogen bonding literature, this was counted as an internal hydrogen bond.¹²² To calculate the probability of forming an internal hydrogen bond (P_{int}), the number of internal hydrogen bonds were summed over all steps at equilibrium and normalized by the maximum number of internal hydrogen bonds possible at equilibrium, assuming that each acid can form one internal hydrogen bond. External hydrogen bonds were determined by considering the distance between the acid group proton and the acid group oxygen and carbonyl oxygen on every other molecule. If this distance was less than 3.3 Å, greater than 1.1 Å, and with a hydrogen bond angle greater than 100°, all commonly employed criteria to determine hydrogen bonds, this was counted as an external hydrogen bond.¹²³ We employed a binary analysis, meaning that each acid molecule received a 0 or 1 value categorizing the presence of an external hydrogen bond, regardless of the number of hydrogen bonds each molecule formed. These values were then similarly normalized by the total number of acid molecules to calculate the probability of forming external hydrogen bonds

(P_{ext}). A molecule can have both internal and external hydrogen bonds at the same time. While additional definitions for hydrogen bonding probabilities are possible, this definition conforms to generally accepted hydrogen bond distances and captures the conformational changes and condensed phase interactions of interest.

Additional conclusions are made by comparing the distributions of I from AIMD simulations to so-called “representative” conformers. These conformers were obtained by randomly selecting ten snapshots from each peak in the AIMD distribution and optimizing them to a local energy minimum using the conjugate gradient method with VASP. I was then calculated using the same protocol as for the AIMD system. To ensure meaningful comparison, only unique conformers – distinguished by backbone bending and acid group rotation – were considered. To ensure consistency between the calculations, key simulation parameters such as the plane-wave cutoff energy, precision settings, functional, and more were kept identical between direct energy minimization and AIMD calculations. The main difference between the two calculation types is the treatment of temperature. The AIMD simulations maintain a constant simulation average temperature at 473K, but the direct energy minimization calculations were optimized at 0 K. This discrepancy may cause small differences in the structures captured by the AIMD and by the direct energy minimization DFT calculations since the AIMD simulations should include structural changes due to thermal fluctuations. However, when varying the simulation average temperature in AIMD, we observed only very slight changes in the conformational distribution (**Fig. B.8**), indicating that any thermally driven structural changes should be negligible. Importantly, we are only comparing the structures between direct energy minimization and AIMD calculations, not the energetics, so we do not

need to worry about the discrepancies in temperature contributions to free energy calculations. See **Fig. B.9** for an example of direct energy minimization with DFT calculation input file.

4.3. Results and discussion

In this study we looked at both saturated and unsaturated DCAs of the same carbon length.

4.3.1. Unsaturated acids

To start, we investigated DCAs that are not fully saturated, namely the *trans*- (FA) and *cis*- (MA) isomers of 1,4-butenedioic acid. Isomerization between the two isomers occurs on timescales much longer than the timescale of conformational changes (fs - ps for conformational changes, seconds - hours for isomerization) and is therefore not thermally accessible in the simulated system.¹²⁴ If these systems were to be studied experimentally, the equilibrium between FA and MA would need to be considered since isomerization, in addition to conformational changes, would be accessible. The focus of this study, however, was exclusively on determining the conformational distribution of FA vs MA rather than on a complete description of conformer and isomer distributions which would introduce additional complexities.

Since we will not observe isomerization in our simulation system, the only structural change we expected to observe for FA is acid group rotation. This rotation leads to a less than 0.5% change in I of FA based on the direct energy minimization calculations (**Fig. 4.2a**). We would not expect to observe such a small structural change in our conformational analysis. Indeed, in AIMD simulations at densities approximating the vapor phase of FA we observed a narrow, unimodal distribution centered at $I = 615 \text{ amu } \text{\AA}^2$ with a standard deviation (σ) of 18 amu $\text{\AA}^2$ (**Fig. 4.2b**). In simulations of FA at condensed phase densities we observed a

distribution centered at slightly higher moment of inertia ($I = 623 \text{ amu } \text{\AA}^2$), but with a similarly narrow σ ($17 \text{ amu } \text{\AA}^2$) (**Fig. 4.2c**), indicating that the vapor and condensed phase systems adopt indistinguishable conformational distributions. Additionally, in both systems we saw a negligibly low P_{int} which substantiates that we will only observe acid group rotations without any backbone bending.

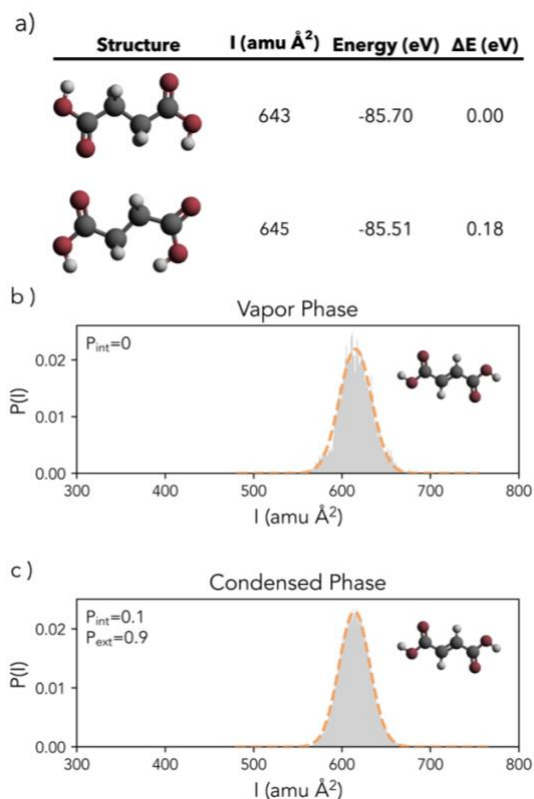


Figure 4.2. a) Representative conformers of FA, identified through direct energy minimization with DFT, with calculated moments of inertia and energies. Moment of inertia distribution, Gaussian fits, and representative predominant structures for vapor (**b**) and condensed phases (**c**) of FA from AIMD simulations.

The lack of intramolecular hydrogen bonding in the simulations at vapor and condensed densities intuitively makes sense, as FA is constrained to the *trans* configuration, restricting interactions between the acid groups within a molecule. Additionally, this geometry allows for

facile intermolecular hydrogen bonding between FA molecules in the condensed phase, due to the availability of hydrogen bond donors and acceptors, leading to a high P_{ext} of 0.9. There was a small population of molecules in the condensed phase, however, which appeared to form donor – acceptor hydrogen bonds of less than 3.3 Å ($P_{int}= 0.1$). Closer observation of the simulation showed that these occurrences were not due to internal H-bonding, but instead due to proton hopping/transfer between FA molecules (**Fig. B.12**). It has been previously observed, both experimentally and theoretically, that protons are highly mobile in carboxylic acids.^{125,126} When protons hop either between molecules or within the same molecule, this is inadvertently captured by the hydrogen bonding analysis, depending on the O-H bond distance (**Fig. B.6** and **B.7**). Proton hopping can contribute to the formation of hydrogen bonding networks or chains, which may delocalize charge throughout the system, and could stabilize the condensed phases of dicarboxylic acids. In other acids with more flexibility, we hypothesize that this phenomenon would promote conformers that can participate in external hydrogen bonding events, like proton hopping, however this is not a consideration for the FA system.

We will also note that the AIMD simulations sample conformations with larger I values than those located by direct energy minimization with DFT. We hypothesize that this is due to the complex potential energy surface which contains a multitude of local minima, some of which with larger I values, which can be accessed with only small structural changes to the acid (e.g. acid group rotation, proton rotation around the acid group, O-H bond elongation, etc.). So, while the minimum energy conformer is the unrotated chain and we cannot differentiate between the two conformers in **Fig. 4.2a** in the AIMD distribution, we would expect that a range of conformations with similar moments of inertia and accessible energies exist in equilibrium in the AIMD simulations, as illustrated by the distribution.

We now turn to MA, the *cis*- isomer of 1,4-butenedioic acid, which maintains the same unsaturated backbone as FA, but which can form internal hydrogen bonds through acid group rotation. Once again, the rotation of these groups leads to a small difference in I , about a 2.5% change from 506 to 493 amu Å² (**Fig. 4.3a**). Consequentially, we observe a unimodal distribution in both the vapor and condensed phase simulations. In the vapor phase, the distribution was centered at 506 amu Å² ($\sigma = 13$ amu Å²) (**Fig. 4.3b**), while in the condensed phase the distribution was centered at 496 amu Å² ($\sigma = 19$ amu Å²) (**Fig. 4.3c**). Furthermore, we observe similar trends to FA when comparing the direct energy minimization and AIMD I values, namely that the AIMD simulations sample acids with larger I values. We can once again hypothesize that these incongruities are driven by a more thorough exploration of the potential energy surface with AIMD.

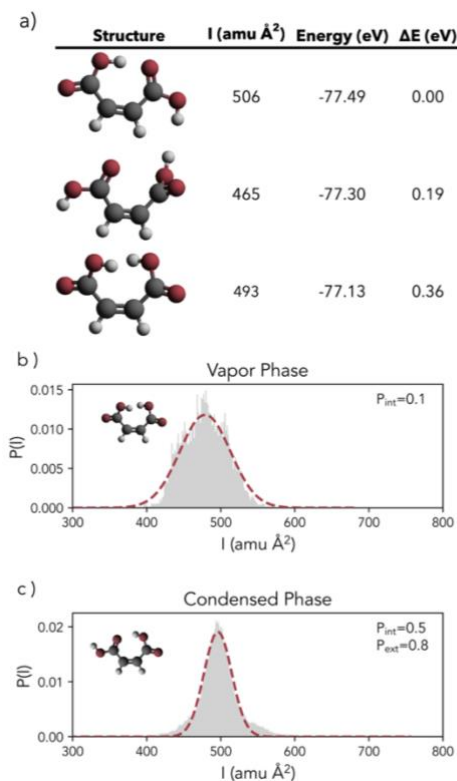


Figure 4.3. a) Representative conformers of MA, identified through direct energy minimization with DFT, with calculated moments of inertia and energies. Moment of inertia distribution, Gaussian fits, and representative predominant structures for vapor **(b)** and condensed phases **(c)** of MA from AIMD simulations.

Unlike with FA, although the I distributions are indistinguishable, we can differentiate between the population of each representative conformer in the AIMD simulation due to their differences in internal hydrogen bonding. As predicted by direct energy minimization, the hydrogen-bonded ring conformer was observed in the vapor phase ($P_{int} = 1$). However, in the condensed phase, MA adopts a mix of conformers as signified by a P_{int} of 0.5. This shift arises from the more complicated energy profile of MA, characterized by multiple structurally and energetically similar conformers, some of which are shown in **Fig. 4.3a**. This complexity results in broader shoulders of the distribution in the condensed phase (**Fig. 4.3c**).

While the hydrogen-bonded ring conformers can only form a one-dimensional chain of externally hydrogen bonded molecules due to the location of their acid groups, the additional conformers have more flexibility in forming external hydrogen bonds and are thus promoted in the condensed phase. This shift in the distribution of conformations corroborates that intermolecular hydrogen bonds stabilize the acid system.

In addition to this conformational diversity, rare proton hopping events also contribute to the high I shoulder observed in the condensed phase distribution. However, the overall fraction of molecules that experience proton hopping over the simulation is low and does not significantly influence the conformational ensemble. These effects are captured in the hydrogen bonding analysis, as proton transfer constitutes a form of dynamic intermolecular interaction. Taken together, the additional conformers and rare proton hopping events further

indicate that direct energy minimization alone may be insufficient for a description of condensed systems with complicated energy profiles, such as those for dicarboxylic acids.

To summarize, we see unimodal conformational distributions from the AIMD simulations of both FA and MA due to the lack of flexibility in the carbon backbone. There are two primary drivers for differences in the distributions from direct energy minimization and AIMD simulations: 1) the sampling of numerous local minima in the potential energy surface which are accessible at equilibrium and 2) the promotion of intermolecular hydrogen bonding which may delocalize charge and stabilize the system. In FA, since acid group rotation doesn't influence interactions, we see that the conformational distribution is uninfluenced by simulation type or phase, indicating that direct energy minimization calculations give a good estimate of the conformer structures present at equilibrium. In MA, however, we observe a promotion of conformers with accessible hydrogen bond donors and acceptors when compared to the vapor phase, leading to a high probability of forming external hydrogen bonds in the condensed phase ($P_{ext} = 0.8$). The complex energy surface of FA and MA conformers, also led to AIMD sampling conformers with larger I values and broader distributions than the idealized conformers calculated with direct energy minimization.

4.3.2. Saturated acids

We applied the same methodology and analysis to SA, the saturated, and thus more flexible, analogue of FA and MA. The flexible backbone of SA increases the degrees of freedom of the system and the number of possible conformations, along with the likely influence of intermolecular and intramolecular interactions in driving different preferred conformers. We categorized the conformers of SA as either ring-like, with $I < 580 \text{ amu } \text{\AA}^2$, or chain-like, with $I > 580 \text{ amu } \text{\AA}^2$ (**Fig. 4.4a**), based on the AIMD distribution and individual

conformer I calculations. The I of the exemplary conformers for these two classes differ by about 25% (e.g. $I = 512 \text{ amu } \text{\AA}^2$ vs $I = 642 \text{ amu } \text{\AA}^2$) which is more significant when compared to the unsaturated molecules discussed in the previous section and distinct enough to be represented by two different peaks in the distribution. Rotation of the acid group within each class of conformer only leads to about a 1% change in I . So, the peak for the ring-like conformer may encompass structures with and without an internal hydrogen bond.

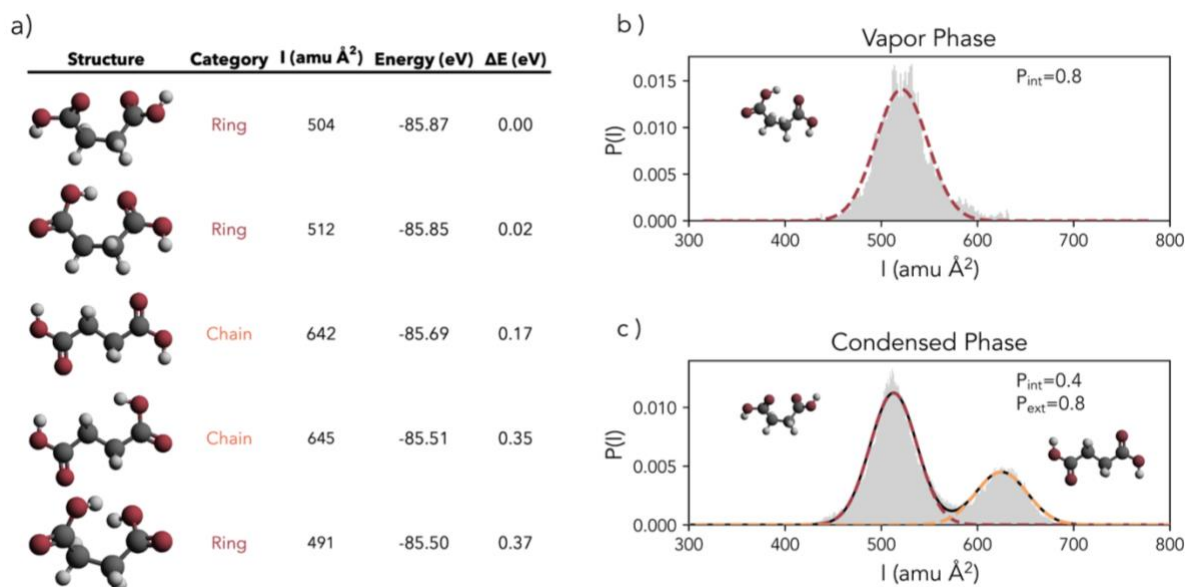


Figure 4.4. a) Representative conformers of SA, identified through direct energy minimization with DFT, with calculated moments of inertia and energies. Moment of inertia distribution, Gaussian fits, and representative predominant structures for vapor (b) and condensed phases (c) of SA from AIMD simulations.

From the direct energy minimization calculations, we would expect SA to exist as a ring conformer in the vapor phase without the influence of intermolecular interactions, since multiple ring conformers are thermally accessible while the chain conformers lie above the thermal energy threshold ($\sim 0.04 \text{ eV}$). Indeed, in the vapor-phase AIMD simulations, we observed a unimodal distribution centered at $521 \text{ amu } \text{\AA}^2$ ($\sigma = 27 \text{ amu } \text{\AA}^2$) (Fig. 4.4b).

Interestingly, although the non-hydrogen bonded ring conformer was the minimum-energy structure per direct energy minimization, we determined that SA exists predominantly in a ring-like structure with an internal hydrogen bond ($P_{int} = 0.8$); since the internally hydrogen bonded structure is within the energy differences due to thermal fluctuations, this structure should be accessible if there is a driving force. This once again demonstrates the stabilizing effect of hydrogen bonds and the limitations in direct energy minimization in fully capturing complex energy surfaces. Since neighbor acid molecules are not available to form intermolecular hydrogen bonds, the vapor phase system adopts conformers with an internal hydrogen bond to delocalize charge.

In the condensed phase, we observed a bimodal distribution of I , with distributions centered at 509 ($\sigma = 25 \text{ amu } \text{\AA}^2$) and 629 amu $\text{\AA}^2$ ($\sigma = 25 \text{ amu } \text{\AA}^2$), consistent with the ring-like and chain-like conformers, respectively (**Fig. 4.4c**). The emergence of chain-like conformers, in which both acid groups are available for external hydrogen bonding, and the mix of ring-like conformers, shown by $P_{int} = 0.4$, demonstrates a shift in the distribution due to the promotion intermolecular interactions. Importantly, the chain-like conformers are not thermally accessible based on the energies calculated by direct energy minimization and thus would not be captured by a simpler analysis of this system. In summary, for both the vapor and condensed phases, we observed conformers that were not predicted to be the minimum energy structures by direct energy minimization, yet that stimulate the formation of stabilizing hydrogen bonds which AIMD is uniquely poised to capture.

When moving from the vapor phase system (density = 0.02 g/cm³) to the condensed phase system (density = 1.2 g/cm³), we observed a shift in the conformational distribution - a decrease in the internal hydrogen bonding probability by an order of two, and a system in which about

80% of the molecules have external hydrogen bonds. To understand the generality of these findings, we compared the distributions and hydrogen bonding probabilities for three different condensed phase systems (density = 1, 1.2, and 1.4 g/cm³) to the vapor and crystal phases (density = 1.62 g/cm³) of SA. As seen in **Fig. 4.5**, there is a linear correlation between the density of the system and the P_{ext} with a slope of 0.6, intercept of 0, and an R^2 of 0.999. The upper bound for this observation should be the crystalline phase for which all SA molecules are externally hydrogen bonded in a chain to form the crystal structure.

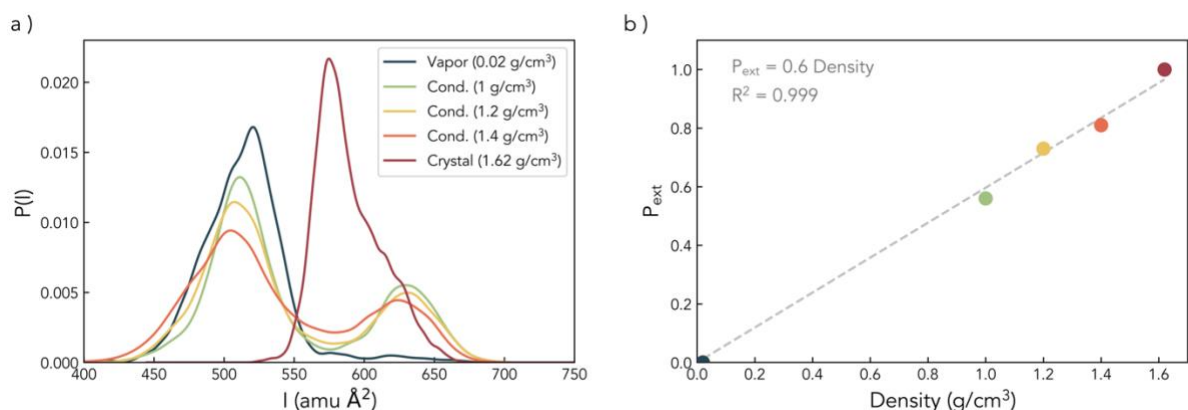


Figure 4.5. a) Moment of inertia distribution of SA with varying density. b) External hydrogen bond probability for SA with varying density.

The effect of density on the conformational distribution of SA is consistent with our overall observation that, when possible, DCAs will adopt conformations that promote either internal or external hydrogen bonds. External hydrogen bonds may stabilize the condensed phase system and are thus promoted in the equilibrium conformational distribution (e.g. MA and SA). We hypothesize that this finding can be applied to systems where the conformational rearrangements required to promote intermolecular interactions are on the same order of magnitude as the stabilizing force of those interactions. For example, with SA, the difference

in the ring and chain conformers is on the order of 0.1 eV and the bond energy of a hydrogen bond is on the order of 0.2 eV.¹²⁷

4.3.3. Connections to experimental trends

Our results show a clear impact of the system environment on hydrogen bond formation and conformations. We illustrate that DCAs tend to increase the strength of the hydrogen bonding framework and the propensity to form chain conformations with increased density. This may be of critical importance for condensed vs vapor phase reactive models for acidolysis and other similar reactions. We compared the conformational distributions calculated in this study with AIMD to acidolysis reactivity trends determined experimentally.

Previous experimental studies found that the rate constants of different DCAs for polyurethane acidolysis in the liquid phase trend with both the number of carbons between acid groups and the ability of the two acid groups to interact.⁸⁹ Since FA, MA, and SA have the same number of carbons in the backbone, we can make predictions about their reactivities based on the likelihood of forming conformations in which the two acid groups can interact in the condensed phase. We would expect that FA would react slowest, as it is locked into the trans configuration, MA would react fastest since it is restricted in the cis configuration, and SA would have a rate constant somewhere in between the two, with the presence of both “ring-like” and “chain-like” conformations per the conformational distribution. Indeed, this is what was determined experimentally, showing that AIMD conformational distributions can be used as predictors for DCA reactivity for specific reactions. However, additional factors, such as acid melting point, may also influence reactivity.

4.4. Conclusions

In this work, we analyzed the conformations and hydrogen bonding probabilities of DCA systems. We utilized this technique to study the effect of molecule rigidity and system density on the molecular structure and interactions by modeling the vapor and condensed phases of fumaric, maleic, and succinic acids. As previously noted, conformations and interactions with the environment can result in drastically different reactivities in a variety of systems. Thus, understanding and quantifying the conformations at relevant reaction conditions is key to accurately predicting chemical reactivities.

By comparing MA, FA, and SA, we showed that intermolecular interactions are promoted in the condensed phase and can influence the external hydrogen bonding probability by a factor of two, which can lead to conformational changes (such as the presence of bimodal conformational distributions, as in SA) and subsequent variations in intramolecular interactions. In FA, both the vapor and condensed phases exist in the same chain-like predominant conformer since its *trans* configuration prevents intramolecular interactions. However, in MA, the predominant conformer changes from an intramolecularly bound molecule in the vapor phase to a mix of molecules with and without internal hydrogen bonds in the condensed phase, as indicated by a change of P_{int} from 1.0 to 0.5. This conformational change was driven by the formation of external hydrogen bonds. We also showed a similar effect in SA. The condensed phase of SA yielded a distinct chain-like conformation that was not observed in the vapor phase and is not predicted to be thermally accessible by direct energy minimization calculations with DFT. The presence of the chain-like conformer and the decrease of P_{int} from 0.8 to 0.4 are again likely due to increased intermolecular interactions in the system. As such, we have demonstrated that for systems with high degrees of freedom and

complex energy surfaces, such as MA and SA, AIMD is necessary to capture the conformational landscape and resulting interactions which cannot be understood through direct energy minimization alone.

Increasing the density of the SA from vapor phase, through the condensed phase, and to the crystalline phase, we see a clear linear relationship between the acid density and the external hydrogen bonding probability (slope of 0.6). This shows that system density could be used to modulate the conformational distribution, and thus the reactivity of the system, towards certain reactions that may be sensitive to conformations.

Lastly, we compared computationally predicted conformational distributions with experimental reactivity trends in polyurethane acidolysis. MA, constrained to a “ring-like” *cis* configuration, exhibits the fastest reactivity. Conversely, FA, limited to a “chain-like” *trans* configuration has the worst reactivity. SA, which accesses both “ring-like” and “chain-like” conformers, shows an intermediate reactivity. These results highlight how conformational flexibility directly impacts reactivity in real systems. Building on this insight, future studies could explore the use of low moment of inertia conformational distributions as predictors for acidolysis reactivity. In addition, incorporating quantum nuclear effects may enhance the accuracy of condensed-phase simulations and increase the frequency of proton transfer events. While such effects are beyond the scope of the present work, they would likely reinforce our conclusion that AIMD simulations are necessary for conformational distributions, particularly for systems with complex hydrogen bonding networks.

5. Mechanistic Origins of Structure-Reactivity Effects in Polyurethane Acidolysis

This chapter is the result of a collaboration with Mahdi M. Abu-Omar (M.M.A.O.), Vojtech Vlcek (V.V), and Phillip Christopher (P.C.). K.R., M.M.A.O, V.V., and P.C. conceptualized the work. K.R. conducted computational studies, analyzed the data, and wrote the paper.

M.M.A.O, V.V., and P.C. provided revisions. V.V. and P.C. supervised the study.

5.1. Main Text

Polyurethane (PU) is the sixth-most produced plastic worldwide, with 21 million tons generated in 2021.¹²⁸ As a crosslinked polymer with high thermal and chemical stability, PU finds use in a variety of industries, from transportation to construction to household applications and beyond.¹²⁹ However, the same properties that make it a useful material also contribute to difficulties in its end-of-life disposal. Less than 20% of PU is mechanically recycled and the rest is landfilled or incinerated.^{77,130,131} Moreover, mechanical recycling typically involves grinding, cutting, or rebinding PU materials into lower value products (e.g. carpet underlay). Acidolysis, a form of chemical recycling that uses carboxylic acid reagents to regenerate the key molecular building block (polyol) has gained recent attention as a more sustainable and circular end-of-life strategy for PU.^{86,90,132–138}

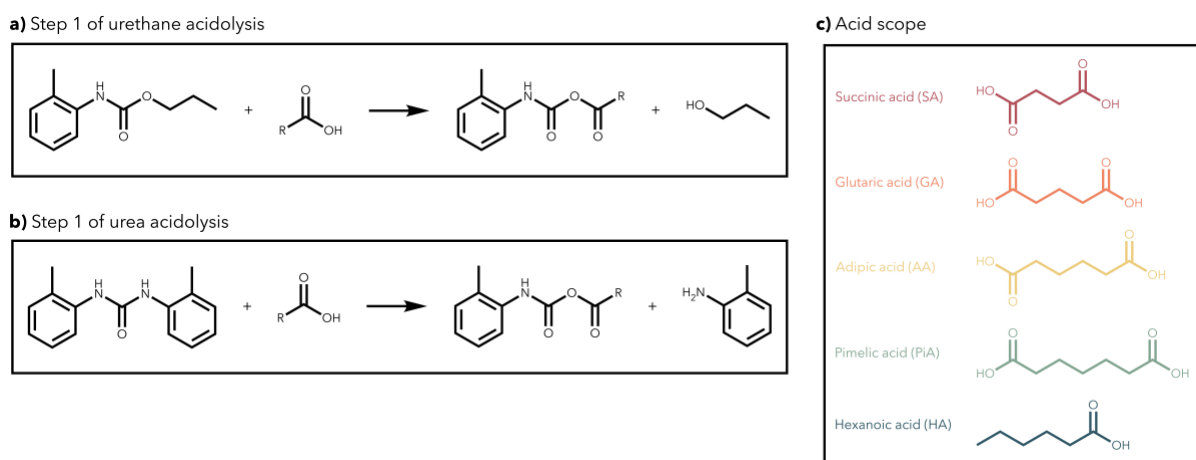
Our prior work has identified two reactivity trends in PU acidolysis: 1) increasing the chain length of dicarboxylic acid (DCA) reagents decreases the apparent rate constant and 2) monocarboxylic acids (MCAs) are slower than comparable DCAs.^{89,139} Notably, these trends are not explained by simple acid strength measurements, such as pKa. We hypothesize that

acid structure and interactions may govern the apparent reactivity. However, the molecular origin of these observed reactivity differences remains unclear. In the previous chapter, we quantified conformational distributions for DCAs, but we lacked a connection between these conformations and reactivity.

Here, we first develop an efficient transition state (TS) generation workflow that samples energetically relevant acid conformers contributing to ensemble averaged reactivity. Then, we use this workflow to develop structure-function relationships for PU acidolysis, grounded in a mechanistic foundation. Improved understanding of the factors governing reactivity can guide the design of more efficient and sustainable PU chemical recycling processes.

Since PU is a large and complex molecule that includes multiple reactive moieties, it is necessary to define a set of model compounds and reactions to represent PU acidolysis. Here, we model PU acidolysis using isolated urethane and urea functionalities to represent the soft and hard domains, respectively (see ref. 13 and **Appendix A** for additional details about the sensitivity to these model compounds). Additionally, we perform these calculations in the gas phase and compare relative trends in reaction energy without including solvation treatment. Although these models do not include long-range ordering or environmental effects, they allow us to isolate the local interactions and intrinsic energetics of individual urethane and urea cleavage steps. Within one reactive system, systematic errors, including those associated with neglecting solvation, are expected to partially cancel in comparisons of relative energies ($\Delta\Delta E$).¹⁴⁰ Thus, while a gas-phase treatment may not reproduce absolute barriers that can be compared to experimental results, it is expected to provide a meaningful description of relative reactivity trends.

The model reactions studied in this paper are acidolysis of urethane (**Scheme 5.1a**) and urea (**Scheme 5.1b**) linkages, both of which are present in PU, using a series of carboxylic acid reagents (**Scheme 5.1c**, 'R' in **Scheme 5.1a** and **5.1b**). The acids were selected to quantify the effect of chain length and carboxyl group number and to enable direct comparison with experimental trends. We focus on the hydrogen-transfer step, previously identified as the rate limiting step.⁸⁹ In this step, the carboxylic acid proton is transferred to the urethane oxygen to form a polyol or to a urea nitrogen to form an amine, yielding a carbamate product in both cases.



Scheme 5.1. Rate limiting step for model urethane (**a**) and urea (**b**) acidolysis. **c**) Carboxylic acid scope for this study.

Flexible molecules such as long-chain carboxylic acids can adopt many conformations with different energies.^{97,99,141} For example, succinic acid (SA) has more than 100 possible conformations based on its torsional flexibility.¹⁴² Modeling acidolysis with a single acid conformation therefore fails to represent the relevant structural ensemble and can bias predicted reactivity. This creates a practical bottleneck for TS studies, since identifying TSs for every energetically accessible conformer is computationally expensive. To capture

conformational effects while accelerating TS searches, we developed a workflow that couples standard computational chemistry tools with TS templates derived from chemical intuition and previously validated TS structures. The templates represent six-membered proton transfer TSs (atoms 1-6 in **Fig. 5.1b, 5.1c**), comprising three reactive atoms from the urethane or urea motif and three from the carboxylic acid. Along the reaction coordinate, the acidic O-H bond (4-3 in **Fig. 5.1b, 5.1c**) is cleaved as the urethane C-O bond (1-2 in **Fig. 5.1b**) or urea C-N bond (1-2 in **Fig. 5.1c**) breaks. Concurrently, the new polyol O-H bond (2-3 in **Fig. 5.1b**) or amine N-H bond (2-3 in **Fig. 5.1c**) forms.¹³⁹

For each acid and reactive group (i.e. urethane and urea), we use RDKit to generate 50 acid conformers (**Fig. 5.1a, step (1)**), optimize their structures and calculate their energies with the Universal Force Field (UFF), select the 10 lowest-energy conformers, and combine each with a urethane (**Fig. 5.1b**) or urea (**Fig. 5.1c**) TS template to generate a TS guess (**Fig. 5.1a, step (2)**).¹⁴³ For DCAs, both acid groups are treated as reactive sites, yielding 20 TS guesses, while MCAs result in 10 structures. Each guess is then optimized with density functional theory (DFT) in Gaussian-16 (PBE0/cc-pVTZ, no solvation) to locate a TS.⁹⁸ All TSs are confirmed to have one imaginary frequency. We then calculate the enthalpic and entropic barriers of the resulting ensemble at 448 K, matching the experimental temperature, using Boltzmann weighting over the conformers and TS structures (**Fig. 5.1a, step (3)**). Here, “ensemble energetic barriers” refer to Boltzmann-weighted averages over the set of conformers and corresponding TS structures accessible at 448 K. In all, this workflow was used to identify 110 TSs to study. Additional details are provided in **Appendix C**. Overall, this workflow automates TS guess generation across conformational space, substantially reducing manual effort while incorporating conformational effects.

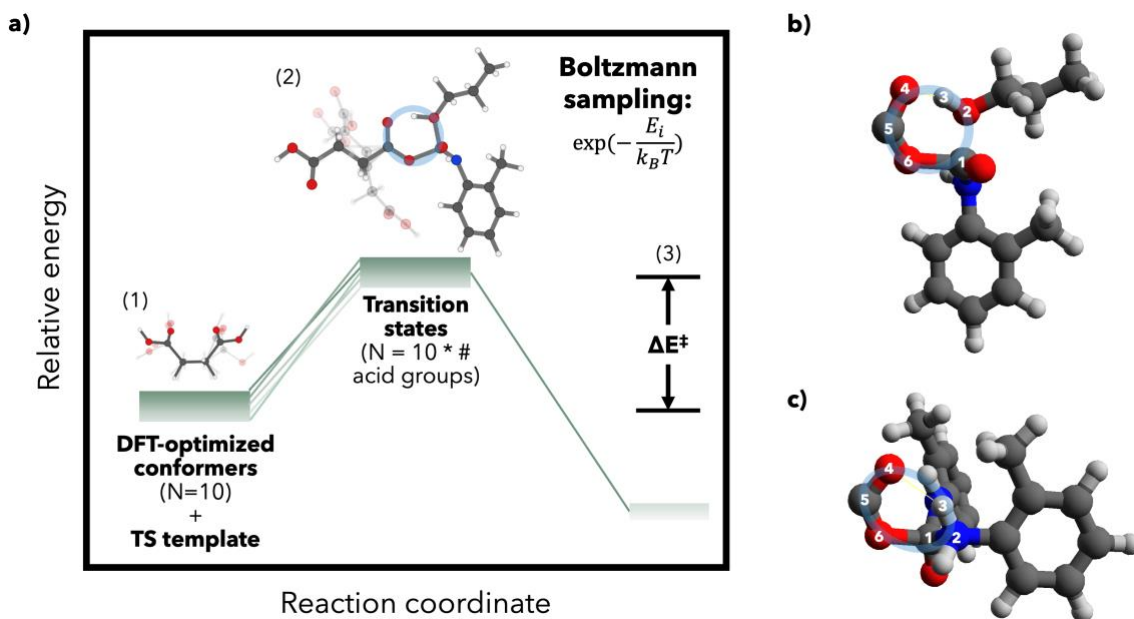


Figure 5.1. a) Potential energy surface generated through TS generation workflow, where shaded bands show conformational distributions included in acid reactant and transition state. Product state is ignored since it does not contribute to the energy barrier. Urethane **(b)** and urea **(c)** transition state templates with the active center marked as atoms 1-6. Atoms 4, 5, and 6 come from the acid. More details can be found in the SI.

From previous experimental studies, we found that urethane cleavage is rate limiting in DCA-mediated acidolysis and that DCA chain length is the best descriptor of urethane acidolysis rates.^{89,139} To investigate the molecular origin of this trend, we utilized our workflow to generate TSs for urethane acidolysis with four DCAs of varying chain length (**Fig. 5.2d**). Although the experimental rate constants decreased $\sim 4\times$ from SA (two carbons between acid groups, $k_{\text{exp}} = 2.16 \mu\text{mol/s}$) to pimelic acid (PiA, five carbons between acid groups, $k_{\text{exp}} = 0.44 \mu\text{mol/s}$), the DFT-calculated ensemble enthalpic barrier, $\Delta H^\ddagger$, spanned from $149 \pm 2 \text{ kJ/mol}$ to $151 \pm 4 \text{ kJ/mol}$, a change of less than 1% across the series (**Fig. 5.2a**). This indicates that the chain-length dependence is not enthalpically driven. Indeed, we observed that the ensemble

entropic barrier, $\Delta S^\ddagger$, decreased from -166 ± 2 J/mol K for SA to -180 ± 1 J/mol K for PiA, equivalent to an increase in $-T\Delta S^\ddagger$ from 74 kJ/mol to 81 kJ/mol (**Fig. 5.2b**). Decomposing the individual contributions to the entropic barrier (rotational, vibrational, and translational) shows that the chain-length dependence is dominated by the rotational term, which accounted for over 50% of $\Delta\Delta S^\ddagger$ across the series (**Fig. C2**). We hypothesize that longer chain acids must pay a larger preorganization penalty to access the TS structure.

From the Boltzmann-weighted $\Delta H^\ddagger$ and $\Delta S^\ddagger$, we used the Eyring equation $k = \frac{\kappa k_B T}{h} e^{\frac{\Delta S^\ddagger}{R}} e^{-\frac{\Delta H^\ddagger}{RT}}$ at $T = 175$ °C to determine a rate constant and normalize this by the maximum calculated value (SA). Our DFT-calculated rate constants ($k_{\text{DFT}}/k_{\text{max}}$) decreased from 1 for SA to 0.23 for PiA (**Fig. 5.2c**), reproducing the experimentally derived trend of a fourfold decrease in acidolysis rate constant and supporting that our model captures the predominant reactivity drivers seen experimentally. We therefore conclude that DCA chain length effects in urethane acidolysis are entropically driven, consistent with longer acids losing more conformational freedom during TS formation.

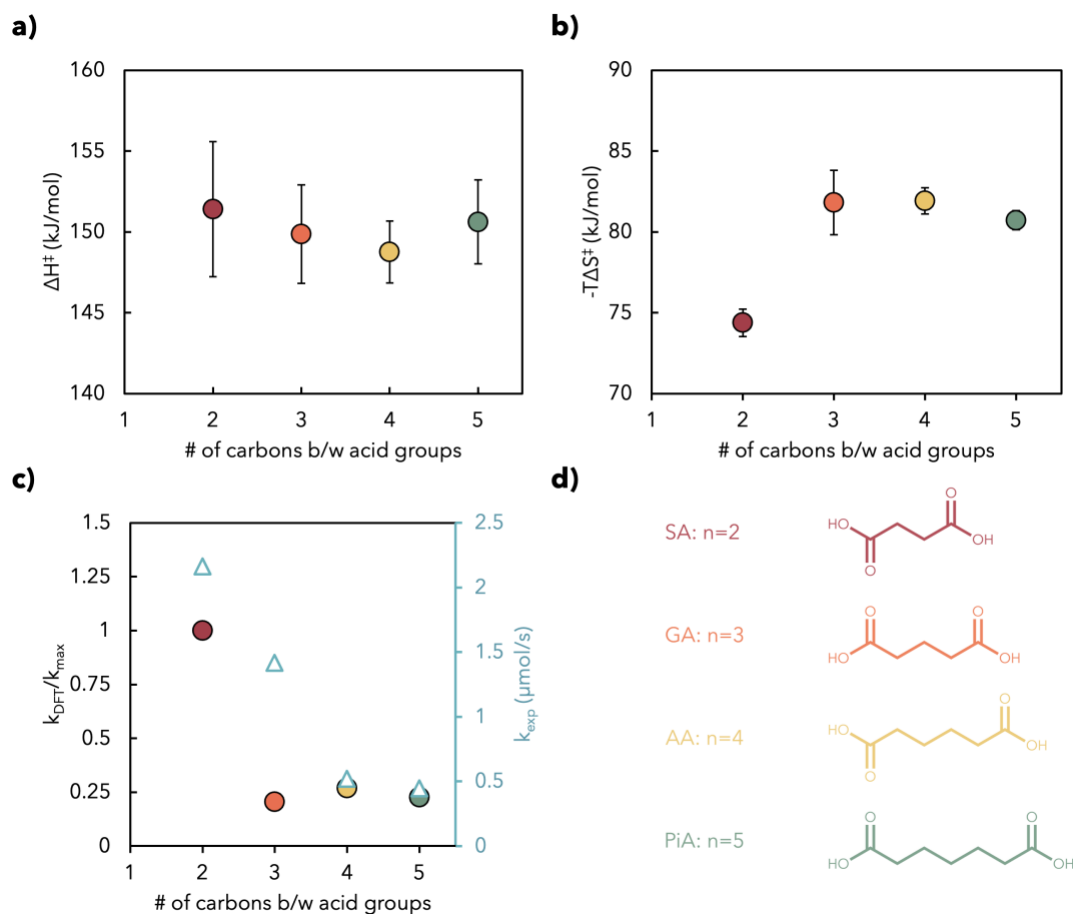


Figure 5.2. a) Enthalpic barrier ($\Delta H^\ddagger$) and b) temperature-weighted entropic barrier ($-T\Delta S^\ddagger$) for urethane acidolysis with DCAs. Error bars represent standard deviations from Boltzmann weighting over acid conformers and TSs. c) DFT-predicted rate constant determined from an Eyring analysis normalized by the maximum value (k_{DFT}/k_{max} , left y-axis, filled circles) compared to experimentally measured rate constant (k_{exp} , right axis, blue triangles). Experimental details: 175°C under inert N_2 atmosphere, 0.5 g PU, saturation acid loadings, see ref. 13 for more details. d) DCA scope where $n = \#$ of carbons between acid groups. Computational details: Gaussian-16, PBE0, cc-pVTZ, $T=448\text{K}$.

Conversely with MCAs, we previously observed that urea acidolysis is rate-limiting and is substantially slower than analogous reactions with DCAs.¹³⁹ For example, while PiA and hexanoic acid (HA) have similar pK_a values (4.48 for PiA and 4.87 for HA at 25 °C) and

comparable backbones (linear aliphatic with a seven (PiA) or six (HA) carbon backbone), HA is about fivefold slower than PiA experimentally ($k_{\text{exp}} = 0.06$ and $0.44 \mu\text{mol/s}$, respectively). However, initial gas phase DFT calculations using our workflow predicted a negligible difference in their enthalpic barriers for urea acidolysis, with $\Delta H^\ddagger = 116 \pm 2 \text{ kJ/mol}$ for both HA and PiA (**Fig. 5.3b**). Experimentally, this is a condensed-phase system with many inter and intramolecular interactions (e.g. PU in contact with a liquid carboxylic acid reagent that acts as both solvent and reactant); our initial DFT calculations, however, omit neighboring functional groups that may facilitate additional interactions.

To assess the role of environmental interactions, we reoptimized the lowest-energy TS and the lowest-energy reacting acid with an explicit hydrogen bonding participant. Since the reaction environment contains abundant polyol functionalities, both within in the PU soft domain and released during depolymerization, we used ethanol as a small alcohol proxy for local polyol hydrogen bonding participants (see **Fig. C.6** for other participants). Under these conditions, PiA $\Delta H^\ddagger$ decreased by 24 kJ/mol to $70 \pm 5 \text{ kJ/mol}$ while the HA $\Delta H^\ddagger$ did not meaningfully change ($115 \pm 3 \text{ kJ/mol}$) (**Fig. 5.3d**). In the stabilized TS, the second carboxyl group on PiA formed two additional hydrogen bonds with ethanol (**Fig. 5.3c**). This stabilization is larger for the TS than for the reactant acid alone, consistent with increased charge separation and polarization in the reactive TS structure. We refrain from quantitative comparisons between these stabilized barriers and experimental values because introducing an explicit hydrogen bonding participant perturbs the entropic contributions in a way that differs between hydrogen-bonded DCA TSs and non-bonded MCA TSs. We therefore used these calculations to assess relative enthalpic stabilization rather than absolute rate predictions.

Although this represents an upper bound on stabilization (additional hydrogen bonding participants introduce competing hydrogen bonds), the qualitative implication is general: the second carboxyl group in DCAs can form favorable hydrogen bonding interactions in the TS while MCAs lack this secondary binding site and stabilization potential. This conclusion is robust to the identity of the hydrogen bond participant used, as similar stabilization in the PiA enthalpic barrier is observed with acetamide, used as a proxy for urea functionalities (**Fig. C.6**). Moreover, introducing ethanol to urethane acidolysis TSs across the DCA series shows the same enthalpic stabilization without disrupting the previously observed chain length dependent entropic trend (**Fig. C.3**). We therefore attribute the slower urea acidolysis with MCAs to a lack of TS enthalpic stabilization in the condensed-phase reaction environment.

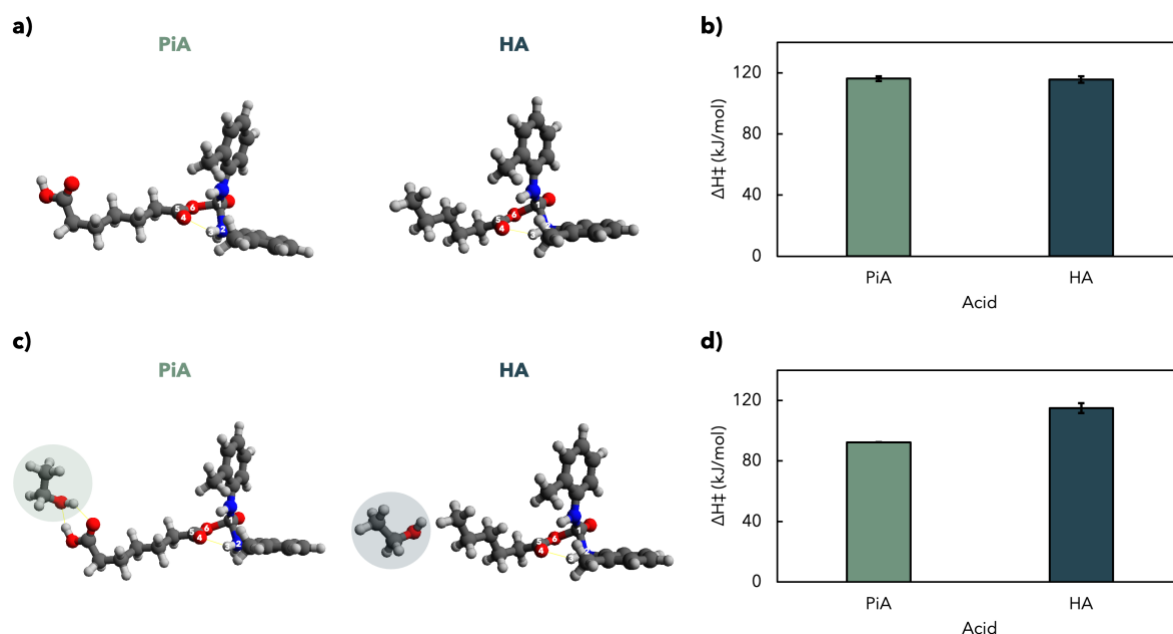


Figure 5.3. Transition states (**a**) and enthalpic barrier (**b**) of urea acidolysis with isolated PiA and HA. Transition states (**c**) and enthalpic barrier (**d**) of urea acidolysis with PiA and HA with an explicit hydrogen-bonding participant (ethanol). Error bars represent standard deviations from Boltzmann

weighting over acid conformers and TSs. Computational details: Gaussian-16, PBE0/ cc-pVTZ, T=448K.

Our computational workflow enables efficient generation of conformational ensembles and Boltzmann-weighted energetic barriers. Using this approach, we calculated the enthalpic and entropic barriers for urethane acidolysis with four DCAs of varying chain length and for urea acidolysis using two acids that differ in carboxyl number (DCA vs MCA), measures that had not been previously resolved. This study required the optimization of over 100 TS structures, each with a distinct initial guess. We estimate that implementing this TS generation workflow reduced manual TS setup time from ~50 hours to ~1 hour. We found that the effect of DCA chain length on urethane is primarily entropic, consistent with a larger conformational/preorganization penalty for longer acids when constrained in the TS structure. In contrast, the reactivity difference between MCAs and DCAs is predominantly enthalpic; DCAs can access additional TS stabilization through intermolecular hydrogen bonding via the non-reacting carboxyl group while MCAs lack this secondary binding site. Together, these results provide insight into previously unexplained experimental observations in PU acidolysis, allowing for more informed selections of reagents in future chemical recycling schemes.

More broadly, these results highlight a general challenge in modeling flexible molecules that can participate in intermolecular interactions: intermolecular stabilization in condensed phase environments, rather than intrinsic barriers, may dominate apparent reactivity. Importantly, our approach quantitatively reproduces the DCA chain-length dependence observed experimentally, indicating that it captures the dominant drivers of reactivity. By contrast, we do not attempt a fully quantitative comparison of MCA and DCA rates because

introducing an explicit hydrogen bonding participant stabilizes DCA TSs but not MCA TSs, leading to non-canceling errors in entropy estimates across the two systems. Incorporating explicit hydrogen bonding networks and heterogeneous reaction environments using QM/MM approaches in which the reaction site (urethane or urea bond with acid group) is treated quantum mechanically while the surrounding reaction environment (e.g. neighboring acids, hard and soft domains) is described with molecular mechanics could address this limitation. Even without fully resolving these heterogeneous reaction environments, our conformationally resolved TS workflow and single hydrogen bonding participant efficiently captures key conformational and environmental stabilization effects, establishing design principles for acid-dependent reactivity trends in PU acidolysis.

6. Glycol-Dependent Kinetics of Uncatalyzed Polyurethane Glycolysis

This chapter is the result of a collaboration with Madeleine Davis (M.D.), Alan L. Stottlemeyer (A.L.S), Christopher Letko (C.L.), Vojtech Vlcek (V.V.), Phillip Christopher (P.C.), and Mahdi M. Abu-Omar (M.M.A.O.). K.R., M.D., A.L.S., C.L., V.V., P.C., and M.M.A.O. conceptualized the work. M.D. conducted experiments. K.R. and M.D. analyzed the data. K.R. completed kinetic fits and computational studies. K.R. wrote this chapter. V.V., P.C., and M.M.A.O provided revisions. P.C. and M.M.A.O supervised the study.

6.1. Introduction

Polyurethane (PU), the sixth most produced plastic worldwide, is synthesized through the polymerization of isocyanates and polyalcohols (polyols). By varying the functionality and relative ratios of these groups, the material and chemical properties of PU can be tuned. Approximately two-thirds of the PU market share is in foam applications, including bedding, furniture, and other consumer and commercial applications, while coatings, adhesives, sealants, and elastomers (CASE) make up the remaining one-third.⁷⁷ All PU materials are chemically and thermally stable, which makes them difficult to mechanically recycle into high-value products. As a result, about 80% of PU waste is landfilled or incinerated.⁷⁷ The remaining share is mechanically recycled into low-value products such as composites or carpet fillers. These limitations highlight the need for more sustainable recovery methods that can restore the polymer's functionality and value.

In contrast to mechanical recycling, chemical recycling uses a chemical cleavage agent to depolymerize the polymer and recover high-value molecular building blocks. Several chemolysis pathways have been explored for PU, including hydrolysis, aminolysis, acidolysis,

and glycolysis. Hydrolysis uses pressurized water or high-temperature steam to cleave PU bonds efficiently, but it is a highly energy intensive process.¹⁴ Aminolysis is the reaction with an amine reagent, generating a complex mixture of polyol, urea, urethane fragments, amines, and other components that requires expensive downstream separations.²³ Acidolysis, which has been commercialized at the pilot scale, uses carboxylic acids to recover polyol. Although acidolysis can proceed to completion within 15 to 60 min depending on the acid used, polyol esterification with excess acid can also occur under reaction conditions, limiting the reusability of the product without further purification.^{89,90}

Among these approaches, glycolysis has recently gained attention because of its relatively mild reaction conditions, high-purity product streams, and strong potential for commercialization.¹⁴⁴ Many prior studies of PU glycolysis have focused on catalyzed systems, employing catalysts such as diethanolamine, sodium hydroxide, or stannous octoate to promote the reaction.^{20,144–147} While De Vos and others have shown that the glycol identity influences the dissolution time and homogeneity of the reaction mixture, a quantitative kinetic understanding of uncatalyzed glycolysis remains unexplored.¹⁷

In this work, we developed an approach to measure polyol release over time during uncatalyzed PU glycolysis. Specifically, we established a protocol to isolate the polyol product and use quantitative ¹³C-NMR and gel permeation chromatography (GPC) to determine the mass of monomeric and oligomeric polyol. We then fit the polyol mass data to first-order rate laws to extract rate constants. Finally, we pair the experimental results of ethylene glycol (EG) to a computational analysis of a wider glycol scope (Glycerol (Gly), EG, 1,3-propanediol (13PD), 1,2-propanediol (12PD), 1,5-pentanediol (15PD), diethylene glycol (DEG), and 2-methyl-1,3-propanediol (2M13PD)) to probe the origin of glycol-dependent kinetics. Overall,

this work establishes a rigorous polyol isolation and kinetic fitting protocol that can be employed for in-depth quantitative studies of PU glycolysis. Note that experimental studies with an expanded glycol scope to improve the kinetic understanding are still in progress.

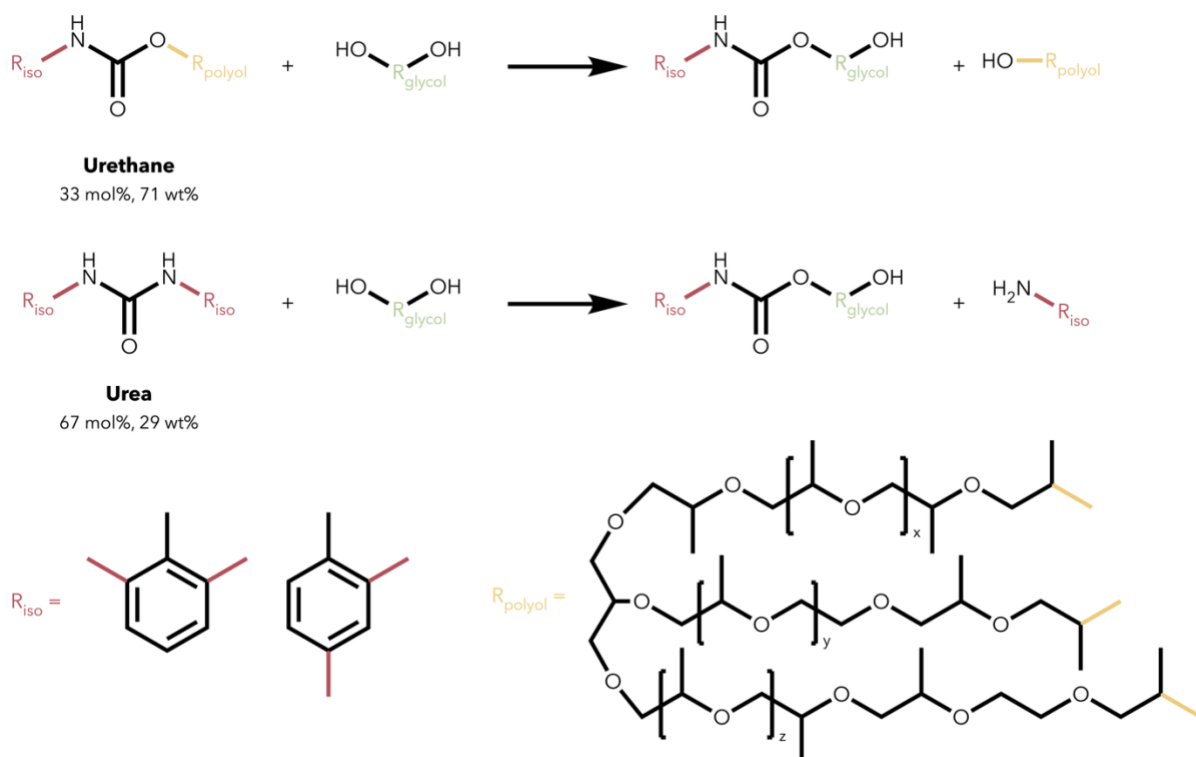
6.2. Methods

6.2.1. Computational

Density functional theory (DFT) calculations were performed to quantify the intrinsic glycolysis reactivity by determining the activation energy for reactions involving Gly, EG, 13PD, 12PD, 15PD, DEG, and 2M13PD. All calculations were carried out using Gaussian-16.⁹⁸ Reactant complexes (glycol and urethane or urea) and transition states (TSs) were optimized using PBE0/cc-pVTZ with GD3BJ dispersion corrections. TS structures were confirmed to have one imaginary frequency and validated with intrinsic reaction coordinate (IRC) calculations.

6.2.2. Experimental

The model PUF (M-PUF) used in this study was synthesized by the Dow Chemical Company using 2,4- and 2,6-toluene diisocyanate (TDI) and VORANOL™ 8136 Polyol, a heteropolymer triol. The resulting PUF theoretically contains 67 mol% urea bonds and 33 mol% urethane bonds, corresponding to 29 wt% urea and 71 wt% urethane linkages. Glycolysis of urethane bonds produces a carbamate and polyol product, while glycolysis of urea bonds produces a carbamate and amine product (**Scheme 6.1**).

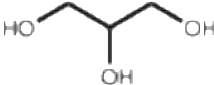
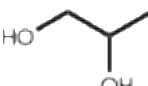
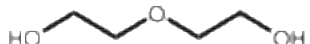


Scheme 6.1. Reaction scheme for glycolysis of urethane bonds (top) and urea bonds (bottom) in M-PUF. Decomposition of urethane bonds forms a carbamate and polyol product. Decomposition of urea bonds forms a carbamate and amine product. The M-PUF was synthesized with TDI (R_{iso}) and VORANOL™ 8136 Polyol (R_{polyol}).

Based on the known foam formulation, complete cleavage of urethane linkages in 1 g of M-PUF yields 0.71 g of polyol, representing the primary mass component. The objective of this study is to determine kinetic parameters for EG and compare these results to computationally derived reactivity trends among a wider scope of glycols (**Table 6.1**). To do this, we performed glycolysis reactions, quenched them at defined time intervals, and isolated the resulting polyol products for analysis.

Table 6.1. Substrate scope for kinetic study of PUF glycolysis with associated physical properties.

Name	Abbrev.	Structure	Boiling point (°C)	Dielectric const.
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Glycerol	Gly		290	46.5
Ethylene glycol	EG		197	37
1,3-propanediol	13PD		210	35
1,2-propanediol	12PD		188	32
Diethylene glycol	DEG		244	32
2-methyl-1,3-propanediol	2Me13PD		214	N/A
1,5-pentanediol	15PD		242	25

Polyol products were isolated using a series of toluene and brine liquid-liquid extractions (**Fig. D.1**). Following reaction completion by quenching in ice water, the reaction flask was washed with toluene and brine, and the combined solution was transferred to a separatory funnel. The solution was gently mixed, resulting in two distinct phases. The majority of the aqueous (brine) phase was removed, and the organic (toluene) layer was centrifuged to promote additional separation of residual aqueous components. Following centrifugation, the remaining aqueous phase was removed and combined with the previously collected aqueous fractions. This extraction procedure was repeated twice with fresh toluene. The collected aqueous phase was washed twice with fresh toluene, followed by the same centrifugation process. After isolation, the combined aqueous phase contained polar products, including residual glycol and carbamate species. The organic phase containing polyol products was dried

to remove solvent, yielding isolated polyol material composed of monomeric and oligomer species.

Quantitative ^{13}C -NMR (qC-NMR) was used to determine the polyol purity of the organic products. Polyol signals corresponding to the propylene oxide backbone were quantified relative to an internal methanol standard (**Fig. D.2**), using chromium (III) acetylacetonate as an added relaxation agent to ensure accurate integration. This method enabled determination of soluble product purity with an estimated uncertainty of 1.5% (**Fig. D.3**). With this analysis, a measured purity of 100% indicates that the isolated soluble material contains entirely polyol monomer or oligomer products.

Gel permeation chromatography (GPC) was used to resolve the distribution of polyol molecular weights. Chromatograms were fit to three Gaussian functions, representing monomer, small oligomers, and large oligomers (**Fig. D.4**). Peak areas were compared to the chromatogram of monomeric VORANOL™ 8136 Polyol standard to determine the mass fractions of monomer and oligomer polyol in the sample (**Fig. D.5**). The overall analytical workflow is summarized in **Fig. 6.1**.



Figure 6.1. Separation and analysis methodology to quantify polyol monomer and oligomer mass of PUF glycolysis products.

6.2.3. Kinetic fitting

Kinetic parameters were determined using a sequential reaction model: $PU \xrightarrow{k_1} \text{oligomer} \xrightarrow{k_2} \text{monomer}$. Rate expressions for oligomer mass $O(t)$ and monomer mass

$M(t)$ are given by **Equations 6.1** and **6.2**, respectively, where U_0 represents the initial amount of monomeric polyol present in the PU. Based on the foam composition, $U_0 = 0.71$ g per 1 g of M-PUF.

$$O(t) = \frac{U_0 k_1}{k_2 - k_1} (e^{-(k_1 + k_2)t} - e^{-2k_2 t}) \quad (6.1)$$

$$M(t) = U_0 [1 - \frac{k_1}{k_2 - k_1} (e^{-(k_1 + k_2)t} - e^{-2k_2 t})] \quad (6.2)$$

For each time point, at least replicate experiments were performed. Oligomer and monomer masses were averaged across replicates prior to fitting. Nonlinear least squares regression was performed in Python, using replicate standard deviations as weighting factors to estimate parameter confidence intervals. Alternative kinetic models were tested and evaluated in **Appendix D**.

6.3. Results and Discussion

6.3.1. Reactivity results

We applied the isolation and analysis protocol outlined above to quantify monomeric and oligomeric polyol formation during PU glycolysis with 15 mL of EG at 190°C (**Fig. 6.2**). Complete dissolution of PU occurred after approximately 1 hr. Samples could not be taken prior to this time as incomplete dissolution would result in underestimation of released polyol (e.g. oligomers not yet solubilized). Because data was obtained only after the maximum oligomer mass had occurred, the initial increase in oligomer concentration was not captured. As a result, large values of k_1 produce similarly good fits, limiting the ability to uniquely determine this parameter. To estimate the lower bound of k_1 , we performed a grid search over k_1 and k_2 and evaluated the resulting fit error (**Fig. D.8**). This analysis indicated that PU to oligomer depolymerization proceeds with a rate constant $k_1 > 1.1 \text{ hr}^{-1}$, while oligomer to

monomer depolymerization exhibited a rate constant $k_2 = 0.2 \text{ hr}^{-1}$. So, this result indicates rapid formation of soluble oligomers followed by significantly slower conversion to monomeric polyol.

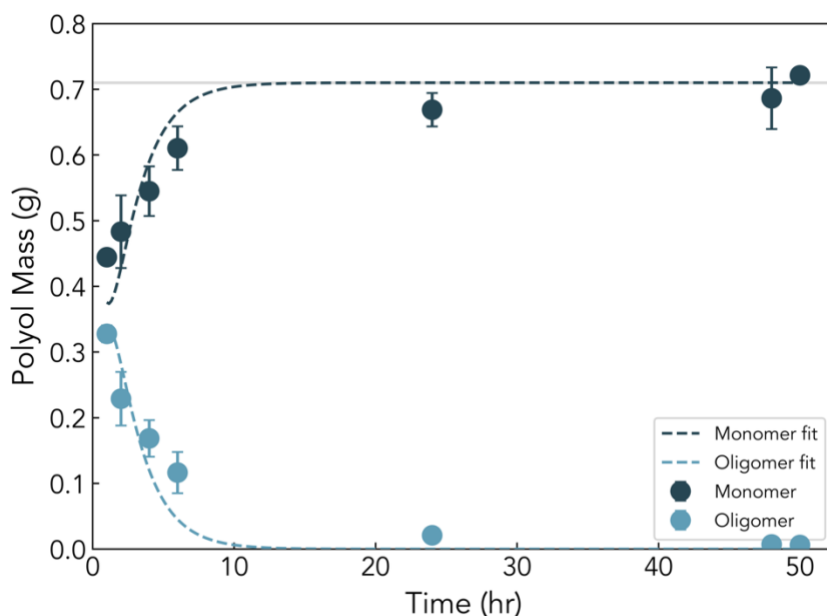


Figure 6.2. Monomeric (dark blue) and oligomeric (light blue) polyol mass evolution and kinetic fits for PU glycolysis with EG. Solid grey line at 0.71 g shows mass of monomeric polyol to be released when all bonds are cleaved. Mass data is fit to Equations 6.1 and 6.2 with a nonlinear least squares regression in Python. Error bars of data points represent standard deviations from replicate experiments. Experimental details: 1 g M-PUF chunk, 15 mL EG, $T=190^{\circ}\text{C}$.

The bond cleavage steps that convert PU into oligomers are chemically analogous to those that convert oligomers into monomers. Therefore, the rates of oligomer (k_1) and monomer (k_2) formation might be expected to be similar, with $k_1 \approx k_2$. Instead, we observe substantial oligomer accumulation, supported by $k_1 > k_2$. Two mechanisms could account for this behavior: 1) mass transport limitations or 2) intrinsic reactivity differences between the two depolymerization steps. From a physical perspective, the reactant initially exists as a solid polymeric network (PUF) which depolymerizes into liquid or soluble oligomers. We therefore

expected these oligomers to be more readily depolymerized than the solid PUF. However, the observed kinetic behavior with EG suggests the opposite, indicating that simple phase accessibility does not explain the larger difference between k_1 and k_2 . Other mass transport effects will be discussed in detail in the next section (6.3.2).

An alternative explanation is that oligomers are initially generated through cleavage of urea bonds within PUF, while formation of monomeric polyol requires subsequent cleavage of urethane bonds within oligomers. If urea glycolysis proceeds more rapidly than urethane glycolysis, this sequence could produce rapid oligomer formation followed by slower monomer production. However, as discussed in **Chapter 3**, urethane cleavage is strongly favored to occur before urea cleavage, regardless of the rate limiting regime, due to bond accessibility within the polymer network.^{94,95} Therefore, intrinsic reactivity differences alone may not fully explain the observed kinetic behavior.

To further evaluate this possibility, we turned to DFT-calculated reaction barriers to predict how urethane and urea intrinsic reactivity varies with glycol polarity.

6.3.2. Computational results

We calculated reaction barriers for urethane and urea glycolysis at 190°C. While barrier trends can be compared within each bond type, the absolute barrier magnitudes for urethane and urea should not be compared directly because they depend on the specific model system used.

Across the glycols studied, the urethane glycolysis barriers remained approximately constant, with an average value of 216 kJ/mol (**Fig. 6.3**, dark blue points). In contrast, urea glycolysis barriers varied modestly with glycol polarity, such that lower-polarity glycols exhibited lower calculated barriers (**Fig. 6.3**, red points). For example, EG, the most polar

glycol tested (dielectric constant = 37), showed a urea glycolysis barrier of 172 kJ/mol while 15PD (dielectric constant = 25) exhibited a lower barrier of 144 kJ/mol. This trend suggests that EG should cleave urea bonds more slowly than the other glycols tested, while less polar glycols such as 15PD should promote faster urea glycolysis. However, preliminary experiments with 15PD show less oligomer accumulation than experiments with EG. Therefore, faster urea glycolysis cannot explain the oligomer accumulation observed with EG.

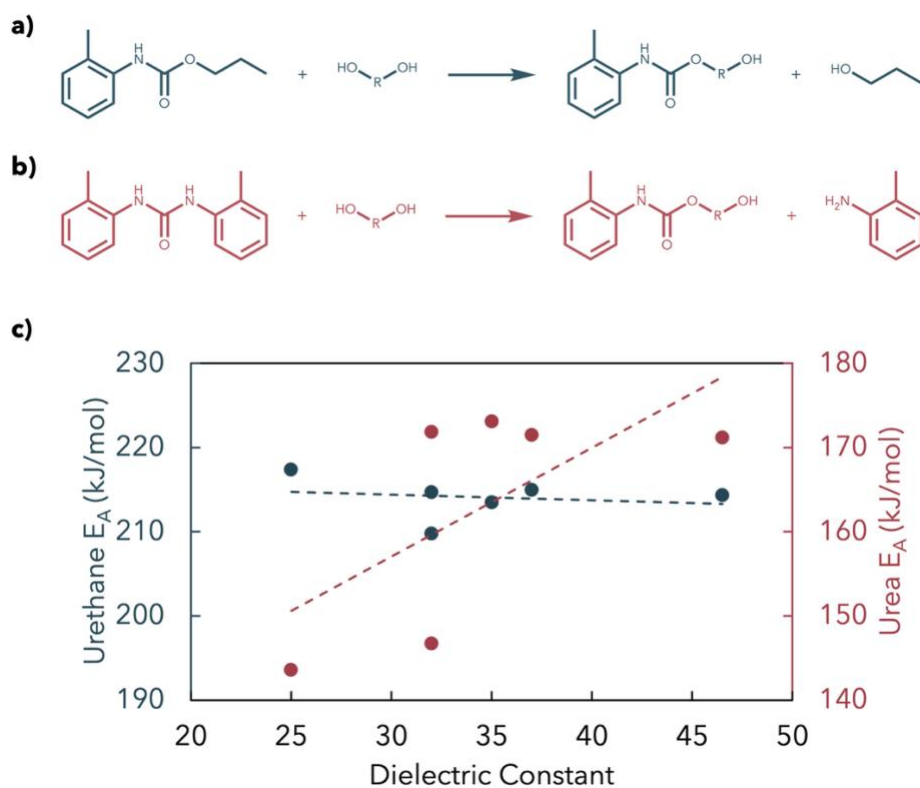


Figure 6.3. a) Model urethane and b) model urea glycolysis reaction schemes. c) DFT-calculated urethane (dark blue, left y-axis) and urea (red, right y-axis) barriers vs dielectric constants for Gly, EG, 13PD, 12PD, DEG, and 15PD. Dashed lines are lines of best fit. Theory details: Gaussian-16, cc-pVTZ/PBE0, GD3BJ dispersion corrections, T=190°C

We therefore hypothesize that polarity mismatch between oligomers and highly polar EG drives the formation of aggregated oligomer structures or chain collapse of larger oligomers. Since oligomers contain relatively nonpolar polyol segments, they may minimize unfavorable

interactions with polar glycols by clustering or collapsing, which would reduce bond accessibility and slow their subsequent conversion to monomer (i.e., reduce k_2). In less polar glycols, reduced polarity mismatch would decrease the driving force for aggregation, improving bond accessibility and accelerating oligomer conversion. Preliminary experimental data from 15PD supports this hypothesis. The maximum oligomer mass observed with 15PD was around 0.1 g, compared to ~0.3 g with EG, consistent with reduced oligomer accumulation in less polar glycols (Fig. D.6). Direct characterization of oligomer aggregation behavior will be required to confirm this mechanism. Moreover, ongoing experimental studies involving additional glycol systems are expected to provide further insight into these effects.

Although glycolysis studies are still preliminary, we can compare the emerging mechanistic picture of PU glycolysis with that of PU acidolysis. In acidolysis, we propose that the rate limiting step can shift between urethane and urea bond cleavage, depending on the number of carboxyl groups in the acid reagent. However, urethane bond acidolysis must occur first because the hard, hydrogen-bonded urea domains may be initially inaccessible. Similarly, in glycolysis, rapid urea cleavage cannot explain the observed reaction behavior, suggesting that urethane bond glycolysis precedes urea bond glycolysis. In this case, however, the reagent character (i.e. glycol polarity) appears to influence the physical behavior of oligomers in solution more strongly than the intrinsic reactivity. Further experimental glycolysis results will help clarify the mechanistic connections between these two reactions. Computational TS comparisons are discussed in **Appendix D**.

6.4. Conclusions and future work

Kinetic parameters are essential for the design and scale up of chemical recycling processes, yet they had not been previously quantified for PU glycolysis. Here, we establish a

rigorous experimental and analytical protocol to determine rate constants for the sequential depolymerization of PU: $PU \xrightarrow{k_1} oligomer \xrightarrow{k_2} monomer$. Using this approach, we determined that $k_1 \gg k_2$ for EG, resulting in substantial oligomer accumulation during the reaction.

Computational results indicate that intrinsic urea reactivity decreases with increasing glycol polarity. Therefore, the experimentally observed kinetic behavior cannot be described solely by intrinsic differences in urethane and urea reactivity. Instead, we propose that the relatively low polarity oligomers are driven to collapse or aggregate in the high polarity EG, reducing bond accessibility for further depolymerization to monomer. Although this aggregation mechanism remains a working hypothesis, it provides a physically consistent explanation for the observed kinetics.

These results establish a foundation for systematic investigation of glycol structure-reactivity relationships in PU glycolysis. With a validated protocol for obtaining reproducible kinetic data, rate constants can now be determined for additional glycols of varying structure and polarity. Such measurements will enable direct testing of the oligomer aggregation hypothesis, particularly if more polar glycols consistently produce greater oligomer accumulation than less polar glycols. Future experimental work should also directly probe oligomer aggregation behavior. Techniques such as dynamic light scattering (DLS) or multi-angle light scattering (MALS) are promising approaches for identifying the presence and size distribution of oligomeric clusters in solution.^{148–150}

Overall, this work provides the first quantitative kinetic description of PU glycolysis and establishes a framework that integrates experimental kinetics with computational reactivity

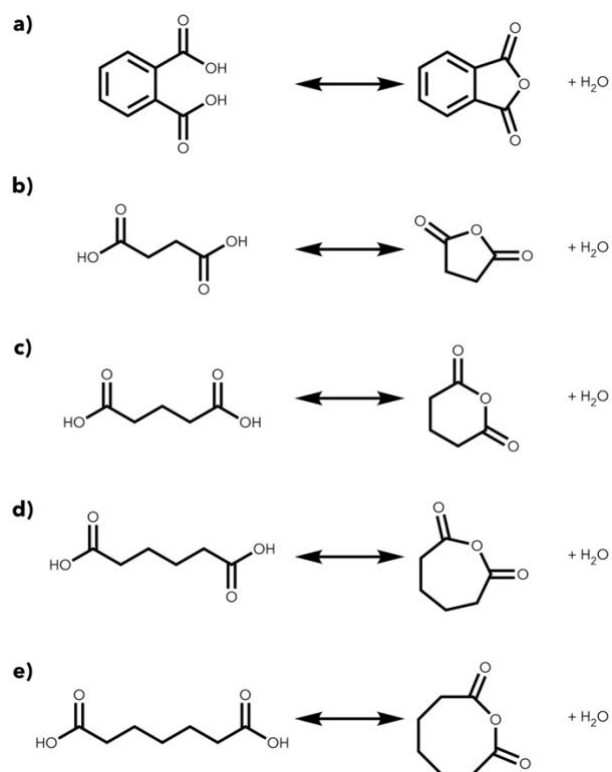
analyses. This combined approach supports future development of scalable PU chemical recycling strategies.

7. Other Studies

The following studies, while distinct and too small to be standalone chapters, all contribute to a deeper understanding of the fundamental processes driving PU chemical recycling. From exploring the energetics of individual steps in acidolysis and glycolysis reactions to understanding the role of acid anhydride formation and PU network morphology, these projects collectively improve our understanding of polyurethane recycling chemistry and ability to design more efficient and selective recycling strategies.

7.1. Acid-Anhydride Equilibrium

We observed experimentally that PUF acidolysis proceeds under three previously unreported conditions: i) under the melting temperature of the DCA, ii) with the acid physically separated from the foam, and iii) with the corresponding acid anhydride physically separated from the foam (which contains trace amounts of water). These observations indicate that the acid vapor and acid anhydride vapor can mediate transport to the foam interface, especially under the melting temperature of the acid. Notably, the anhydride exhibits higher apparent reactivity than the acid, consistent with its high vapor pressure and thus greater concentration in the vapor phase. However, the thermodynamic equilibrium between DCAs and their corresponding anhydrides under reactions conditions is unknown (**Scheme 7.1**).



Scheme 7.1. Acid-anhydride equilibrium of a) phthalic acid (PA), b) SA, c), GA, d) AA, and e) PiA

To quantify this equilibrium, we used DFT to calculate the free energies of both acid and anhydride species at relevant temperatures. The equilibrium constant was determined from $\Delta G = -RT \ln(K)$ using optimized structures of the minimum energy acid conformers identified in **Chapter 5**. **Fig. 7.1** summarizes the calculated equilibrium constants at 175°C (PBE0/cc-pVTZ, GD3BJ).

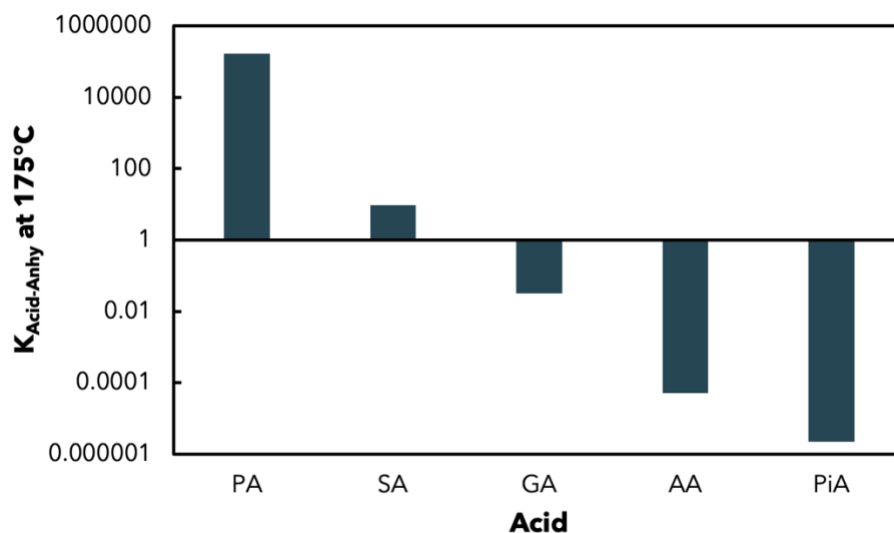


Figure 7.1. DFT-calculated acid-anhydride equilibrium constant at 175°C with PA, SA, GA, AA, and PiA. Theory details: PBE0/cc-pVTZ, GD3BJ, T=175°C.

These results reveal a strong dependence of the acid-anhydride equilibrium constant on chain length. Short chain acids favor anhydride formation while longer chain acids favor the acid form. Specifically, phthalic acid (PA) and SA exhibit equilibrium constants greater than one ($K \sim 1.5 \times 10^5$ for PA and $K \sim 10$ for SA), indicating that the anhydride is thermodynamically favored under reaction conditions. In contrast, GA, AA, and PiA show equilibrium constants significantly less than one ($K \sim 3 \times 10^{-2}$ for GA, 5×10^{-5} for AA, and 2×10^{-6} for PiA), indicating a thermodynamic preference for the acid form.

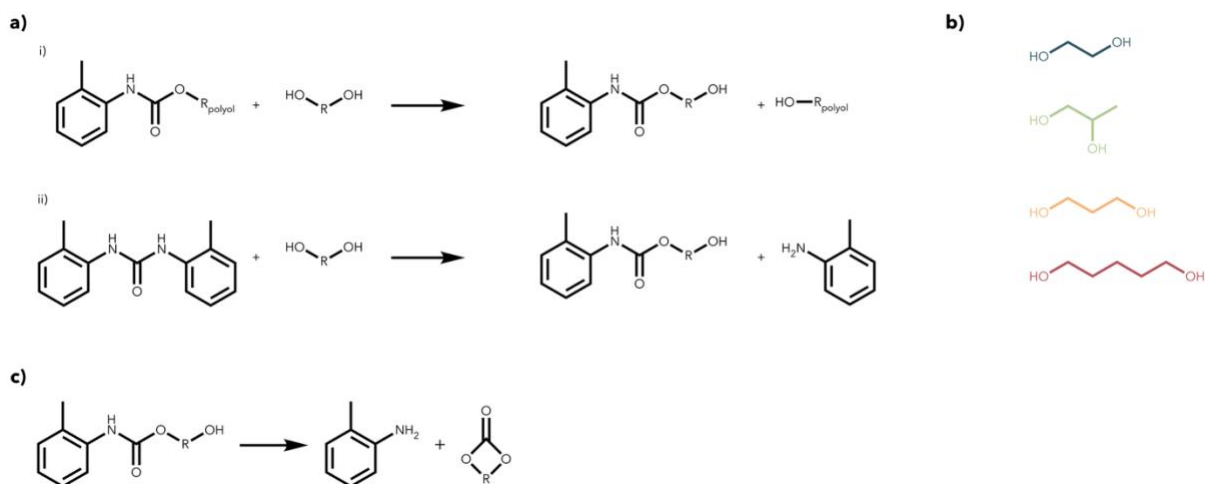
These thermodynamic trends correlate with experimentally observed reactivity. PA and SA, which favor anhydride formation, also exhibit the highest acidolysis rates and are hypothesized to reach the PUF surface predominantly via the vapor phase. While the acid melting temperature and conformational effects (**Chapters 4 and 5**) may also contribute to these effects, the predominance of the volatile and mobile anhydride species likely enhances effective transport and contributes to the increased apparent reactivity. Conversely, GA, AA, and PiA remain primarily in the acid form at reaction temperatures (165-195°C), which are

above their melting points, suggesting that transport occurs predominantly through the liquid phase. These results identify acid-anhydride thermodynamics as an additional chain length dependent factor governing acidolysis reactivity, alongside previously established kinetic and conformational effects

7.2. Carbamate to CO₂

During glycolysis, we observe significant CO₂ evolution. This observation is inconsistent with the expected reaction pathway, in which the reaction of glycol with urethane produces a polyol and carbonate species, without gas evolution (**Scheme 7.2a**). Prior studies have attributed gas formation during PU glycolysis to either hydrolysis or thermal decomposition of the PU.^{15,145} However, thermogravimetric analysis (TGA) showed that the PUF thermal decomposition occurs above ~210°C and the addition of water did not affect the rate or extent of gas evolution, thus excluding these proposed CO₂ formation routes.¹²

Interestingly, gas evolution coincides with the disappearance of the carbamate species as observed in the ¹H-NMR spectra, indicating a direct relationship between carbamate consumption and gas formation. Notably, both the CO₂ production and the carbamate disappearance are strongly dependent on glycol identity (**Scheme 7.2b**). Specifically, ethylene glycol (EG) and 1,2-propanediol (12PD) exhibit substantial CO₂ evolution, while 1,3-propanediol (13PD) and 1,5-pentanediol (15PD) show negligible gas formation. Based on these observations, we propose a reaction pathway in which the carbamate forms a cyclic carbonate intermediate which later decomposes to release CO₂ (**Scheme 7.2c**).



Scheme 7.2. a) Glycolysis of i) urethane and ii) urea. b) Glycol scope, from top to bottom: EG, 12PD, 13PD, and 15PD. c) Hypothesized carbamate to cyclic carbonate and amine reaction.

To evaluate this hypothesis, we computed the reaction free energies (ΔG) and optimized cyclic carbonate structures for each glycol (PBE0/cc-pVTZ, GD3BJ, $T=190^\circ\text{C}$). As shown in Fig. 7.2a, this reaction is thermodynamically favorable for EG and 12PD ($\Delta G = -31$ kJ/mol and -42 kJ/mol, respectively) but significantly less favorable for 13PD and 15PD ($\Delta G = -11$ kJ/mol and 4 kJ/mol, respectively). We additionally quantified ring strain in the cyclic carbonate intermediates by comparing the C-O-C bond angle to the ideal bond angle (109.5°) (Fig. 7.2b). For EG and 12PD, the deviation from the ideal angle is $<1^\circ$, indicating minimal strain. In contrast, 13PD and 15PD exhibit deviations greater 6° , consistent with increased ring strain and reduced stability of the cyclic intermediate.

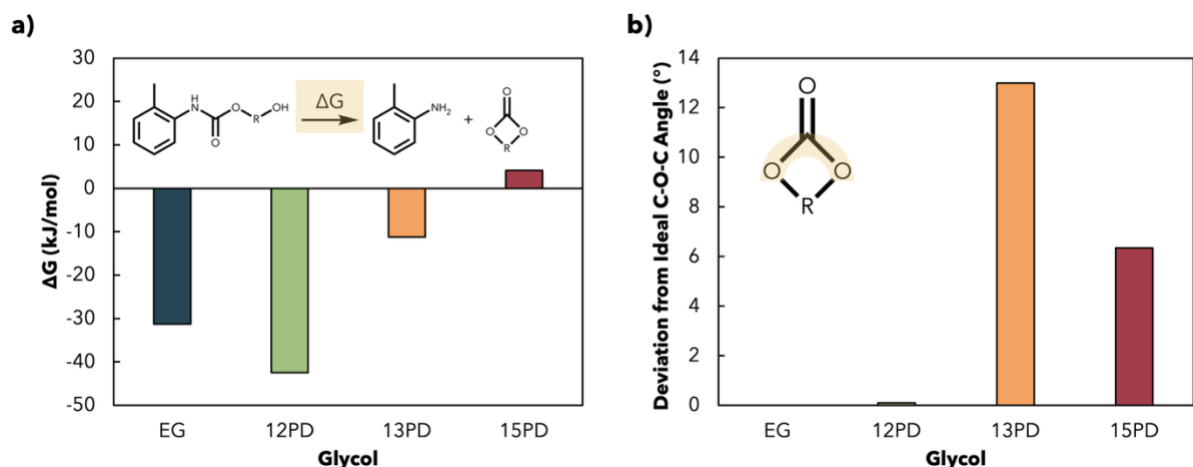


Figure 7.2. a) Reaction free energy of carbamate to cyclic carbonate reaction for EG, 12PD, 13PD, and 15PD. b) C-O-C bond angle in cyclic carbonate as compared to a 109.5° bond angle for EG, 12PD, 13PD, and 15PD. Theory details: PBE0/cc-pVTZ, GD3BJ, T=190°C.

Together, these results support a mechanism in which CO_2 formation proceeds via carbamate cyclization to a cyclic carbonate intermediate, rather than through hydrolysis or thermal decomposition. The agreement between experimental trends and computed thermodynamics indicates that this pathway is both energetically and structurally controlled. Specifically, glycols capable of forming low-strain cyclic intermediates (EG and 12PD) promote CO_2 evolution while glycols that experience geometric constraints suppress this pathway.

7.3. Glycol-PUF Contact Angle Measurements

In both glycolysis and acidolysis of PUF, experimentally measured reaction rates represent apparent kinetics that could involve a convolution of both intrinsic chemical reactivity and mass transport limitations. The chemolysis reagent and PU interactions are expected to influence the extent and rate of PU dissolution and intercalation into the polymer network. Several of our hypotheses regarding the glycol dependent reactivity trends involve differences

in glycol and PUF compatibility, which are expected to vary with glycol polarity. However, the relationship between glycol polarity and PU domain miscibility has not been previously quantified.

To evaluate this effect, we measured static contact angles between glycol droplets and the PUF surface for glycerol, ethylene glycol (EG), 1,3-propanediol (13PD), and 1,5-pentanediol (15PD) (**Fig. 7.3a**). A needle syringe was used to add a single drop of glycol onto a surface of an approximately 2 cm x 2 cm x 3 cm chunk of model PUF. Contact angles were determined from both the left and right droplet profiles and averaged after 1 min of equilibration on the PUF surface. Each reported value represents the mean of four independent measurements taken from different locations on the surface (**Fig. 7.3b**). All measurements were collected using the ramé-hart model 100-25-A goniometer.

From this analysis, we observe that the measured contact angles exhibit a systematic dependence on glycol polarity. Highly polar glycols (e.g. glycerol: 113°, EG: 91°) exhibit the largest contact angles, indicating reduced wetting of the PUF surface. In contrast, less polar glycols (e.g. 1,5-pentanediol: 70°) exhibit smaller contact angles, consistent with improved wetting of the PUF surface. This trend is further illustrated in **Fig. 7.3c**, where contact angle decreases approximately linearly ($R^2=0.94$) with decreasing dielectric constant of the glycol.

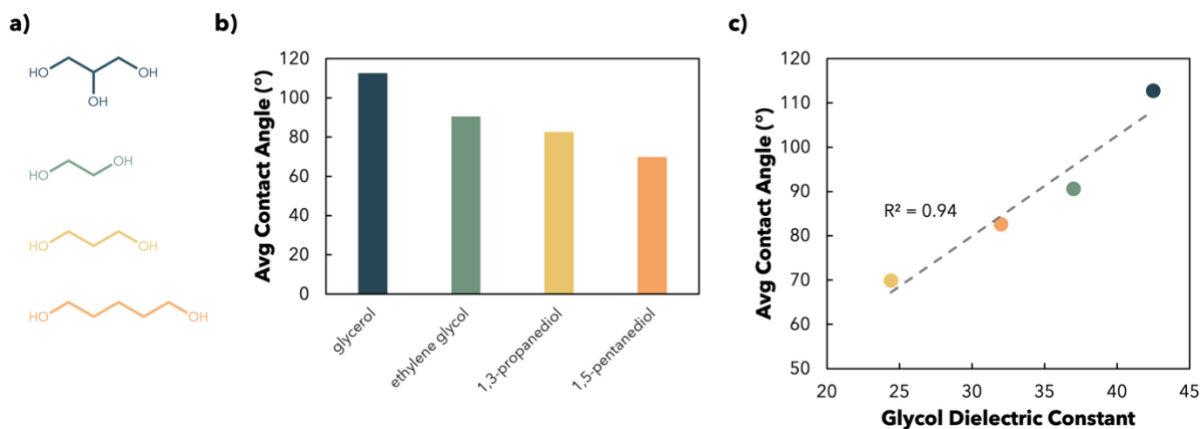


Figure 7.3. a) Structure of glycols studied. b) Average contact angle of a glycol drop on a PUF surface. Averaged between left and right sides and over four replicate experiments. c) Average contact angle of a glycol drop on a PUF surface vs the glycol dielectric constant. Taken on ramé-hart model 100-25-A goniometer.

These results indicate that the PUF surface exhibits relatively low polarity, consistent with the presence of soft domains composed primarily of low polarity polyol segments. Reduced wetting by highly polar glycols suggests limited interfacial contact and potentially reduced diffusion into less polar regions of the polymer network. Conversely, less polar glycols exhibit improved wetting, which may enhance intercalation into soft domains and increase the accessibility of urethane linkages. It's important to note, however, that contact angle measurements are typically performed on smooth, planar, and chemically homogenous surfaces, unlike PUF, which presents a rough and porous interface with a heterogeneous local structure (**Fig. 7.4**). As a result, the measured values should be interpreted as apparent contact angles influenced by surface morphology rather than precise wetting angles. Accordingly, these data are most useful for identifying relative trends in intercalation behavior across the glycol series, rather than for assigning quantitative contact angles.



Figure 7.4. Photo of PUF surface, taken on ramé-hart model 100-00 goniometer, showing heterogeneity of surface used in contact angle measurements.

7.4. PUF Morphology

Previous experimental observations have led us to two hypotheses associated with the spatial accessibility of urethane and urea bonds: i) urethane bonds can be preferentially cleaved prior to significant urea bond decomposition (**Chapter 3**) and ii) high molecular weight polyol oligomers can be released quickly compared to slower monomeric polyol release (**Chapter 6**). Molecular scale descriptions of urethane and urea accessibility remain limited. The object of this section is to develop a structural model that captures the spatial organization of functional groups within PU, providing a framework for interpreting reactivity trends.

Using the experimentally relevant PUF composition (33 mol% urethane bonds and 67 mol% urea bonds), we developed a computational workflow to construct representative PU network topologies. The model enforces stoichiometric and connectivity restraints: i) urea bonds form between two isocyanate groups, ii) urethane bonds form between isocyanate and polyol groups, iii) each polyol node forms three urethane bonds, and iv) each isocyanate node forms a maximum of two bonds. For a specified total number of bonds, the required numbers of isocyanate and polyol nodes are calculated and randomly distributed in three-dimensional space. Then, bonds are assigned between these nodes, subject to the previously reported constraints and the experimentally relevant urea and urethane content. The resulting network provides a statistical representation of possible spatial arrangements of urethane and urea domains.

Several structural features emerge from this model. First, even at relatively small system sizes (e.g. 200 bonds in **Fig. 7.5**), PU exhibits complex topology, including loops, dead ends, and heterogeneous connectivity. Second, the model predicts extended sequences of urea bonds. These segments are consistent with the formation of hard domains in PUF and are expected to

exhibit reduced accessibility due to dense packing and intermolecular interactions.^{94,95} This provides a structural basis for the experimentally observed urethane bond cleavage prior to urea bond decomposition (**Chapter 3**). And third, polyol rich regions form localized clusters connected by urethane and limited urea linkages. We hypothesize that scission of the surrounding bonds could release these clusters as oligomeric species, while further depolymerization to monomers would require cleavage of additional, potentially less accessible, linkages connecting them. This interpretation is consistent with the observed rapid release of oligomers and slower formation of monomeric polyol (**Chapter 6**).

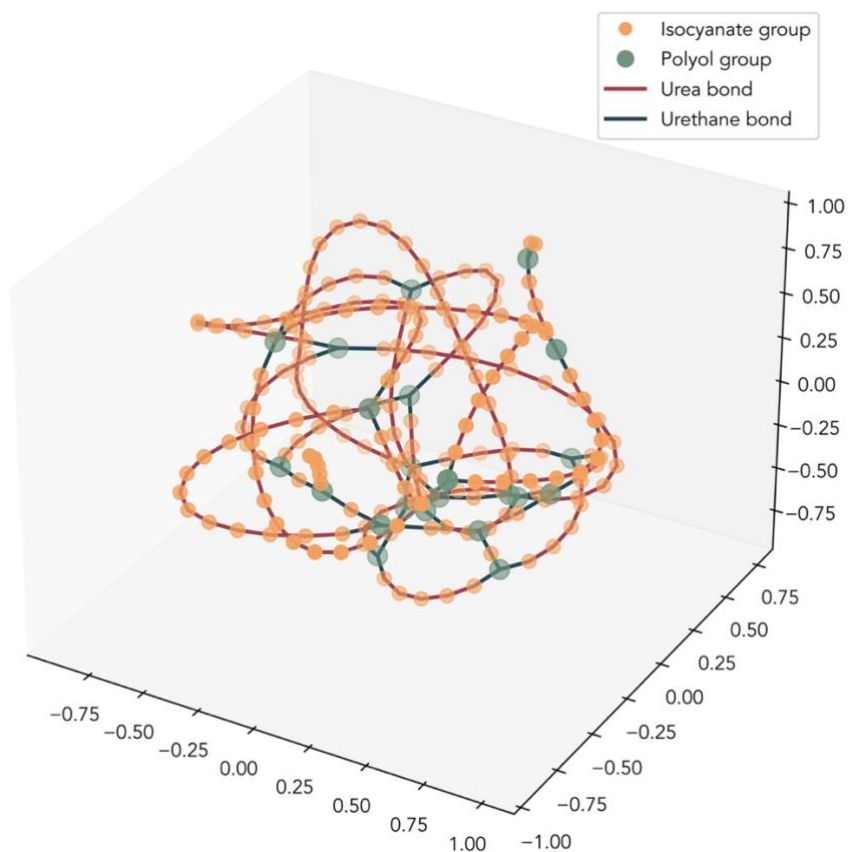


Figure 7.5. Simulated PU network constructed by enforcing connectivity and composition constraints showing isocyanate nodes (orange), polyol nodes (green), urea bonds (red lines), and urethane bonds (blue lines).

It is important to note that this model is intentionally simplified. It neglects intermolecular interactions (e.g. hydrogen bonds), steric constraints due to realistic bond angles and dihedrals, and other energetic considerations. As such, the model should be interpreted as a topological rather than an atomistically accurate representation. A more physically realistic description would require coarse-grained molecular dynamics simulations capable of incorporating nonbonded interactions. While initial steps toward defining a coarse-grained representation were started, a full implementation is beyond the scope of this dissertation.

8. Conclusions

8.1. Summary

Polyurethane (PU), the sixth most produced plastic globally, is widely used as flexible foam synthesized from polyol, isocyanate, and water to form a thermoset polymer containing urethane and urea bonds. Due to its high thermal and chemical stability, PU is difficult to mechanically recycle while preserving its material value. Instead, traditional mechanical recycling typically produces low-value products with limited applicability, motivating the need for alternative end-of-life pathways that maintain the utility of the original PU material. Acidolysis and glycolysis are two promising chemical recycling pathways that cleave PU into polyol and nitrogen containing products. However, limited kinetic and mechanistic understanding of these reactions has limited industrial implementation.

This dissertation combined computational chemistry and kinetic modeling to probe the molecular origins of reactivity in PU acidolysis and glycolysis. **Chapter 2** described the theoretical framework and computational tools used throughout this work. These tools enabled a systematic mechanistic investigation of acidolysis, including variations in reagent electrophilicity, chain length, and carboxyl group number, followed by initial mechanistic studies of glycolysis, focusing on the role of glycol polarity.

Chapter 3 established the electronic origins of reactivity differences between urethane and urea bonds during acidolysis. Using benzoic acid and its electronic analogues, depolymerization was tracked using gas evolution, GPC, and NMR measurements. These results revealed biphasic kinetic behavior characterized by rapid urethane bond cleavage and slower urea acidolysis. Urethane rates were insensitive to electronic modifications to benzoic acid, while urea depolymerization rates strongly correlated with acid electrophilicity, yielding

a Hammett reaction constant of $\rho=3.00 \pm 0.01$. Density functional theory calculations revealed that this sensitivity arose from bond elongation and charge delocalization in the urea transition state, which was minimized in urethane acidolysis.

Chapter 4 addressed the role of conformational complexity in dicarboxylic acid systems. Flexible DCA molecules often adopt multiple conformations with distinct energies and reactivities, requiring characterization of their full conformational free energy landscape. Traditional computational studies using direct energy minimization with DFT fail to fully capture the conformational distribution, particularly condensed phase effects. AIMD simulations revealed additional thermally accessible conformers stabilized by intermolecular interactions, namely external hydrogen bonding in the condensed phase. Increasing system density promoted these interactions and shifted conformational populations. These predicted conformational distributions correlated with experimental reactivity, where acids more likely to form ring-like conformations exhibited faster acidolysis rates.

While AIMD can reveal key information about the equilibrium conformations of acids, it does not elucidate reactivity information. **Chapter 5** described a workflow to rapidly generate and optimize acidolysis TSs with DFT and used it to rationalize experimentally observed trends in acid chain length and carboxyl group number. Chain-length effects were found to be entropically driven, with longer acids incurring a greater preorganization penalty in the TS. Differences between MCAs and DCAs were primarily enthalpic, as DCAs accessed additional TS stabilization through hydrogen bonding involving the second carboxyl group. Together, these results established molecular design principles governing acid-dependent reactivity in PU acidolysis.

Following completion of the acidolysis studies, **Chapter 6** focused on glycolysis, a similarly promising chemical recycling pathway that lacked quantitative kinetic information. A new experimental and analytical method was developed to quantify monomeric and oligomeric polyol formation over time using isolated reaction products analyzed by qC-NMR and GPC. Application of this method to EG revealed significant oligomer accumulation, indicating that the conversion of PU to oligomer proceeds rapidly relative to oligomer to monomer depolymerization. Comparison to DFT-calculated activation barriers indicated that intrinsic reactivity differences alone could not explain the observed kinetics, suggesting that transport effects, such as polarity-driven aggregation, govern oligomer reactivity.

In addition to the primary studies described above, **Chapter 7** presented supporting investigations that further expand mechanistic understanding of PU chemical recycling. These studies include calculation of acid-anhydride equilibrium constants across DCAs of varying chain lengths, identification of a cyclic carbonate intermediate that participates in CO₂ formation during glycolysis, measurement of glycol wetting behavior on PU surfaces through contact angle analysis, and development of graph network representation of PU morphology at experimentally relevant compositions.

Collectively, this dissertation establishes a mechanistic framework, connecting molecular-scale reactivity to macroscopic depolymerization behavior in PU chemical recycling. By integrating computational modeling with experimental kinetics, these studies provide new insight into the roles of electronic structure, molecular conformations, hydrogen bonding, and transport phenomena in governing PU depolymerization.

8.2. Outlook

Additional computational studies in PU chemical recycling can advance the field by refining existing modeling techniques and extending these tools to new reaction systems.

8.2.1. Improvements to modeling techniques

Throughout this dissertation, significant effort was made to capture key features of the experimental system with computational models, including implicit solvation in **Chapter 3**, condensed phase environments in **Chapter 4**, and conformational variability in **Chapter 5**. These approaches enabled isolation of the dominant molecular factors governing reactivity while maintaining tractable computational cost. However, simultaneously capturing all experimentally relevant features, such as bifunctional urethane and urea morphology, neighboring chemical moieties that contribute to intermolecular interactions, and condensed phase reagent environments with fluctuating conformations, remains computationally challenging within a fully quantum mechanical framework.

One promising pathway for extending these models is the use of hybrid quantum mechanical/molecular mechanical (QM/MM) methods. In this framework, the reactive region (e.g., the urethane or urea bond and the interacting acid or glycol molecule) is treated quantum mechanically while the surrounding polymer matrix and condensed-phase environment are described using molecular mechanics. This partitioning significantly reduces computational cost while enabling explicit representation of neighboring interactions and local morphology.

Implementation of QM/MM methods for PU recycling systems would require MM models capable of accurately representing PU chemistry and associated reagents. Fortunately, many well-established general purpose force fields exist, and recent advances in active-learning based parameterization provide new opportunities to efficiently develop system-specific force

fields. However, successful application of these approaches would still require substantial effort in force-field development, parameterization, and validation.

Such approaches offer the potential to extend the mechanistic insights developed in this work by incorporating conformational, hydrogen bonding, and morphological effects within a unified simulation framework. Improved representation of these features would further enhance predictive reactivity modeling and support the design of more efficient and selective chemical recycling processes.

8.2.2. Application of workflow to new systems

This dissertation established a mechanistic framework for modeling PU acidolysis, including reaction barrier calculations across a diverse set of acids for both urea and urethane bond cleavage. While this dissertation provided detailed insight into acidolysis reactivity, similar foundational knowledge remains limited for many other PU chemical recycling pathways. The computational workflows developed here are broadly transferable and can be applied to identify molecular drivers governing other depolymerization behavior.

Chapter 6 established an initial understanding of reactivity drivers in glycolysis, demonstrating how reaction barriers vary with glycol polarity. However, additional structural factors remain to be explored. Glycols are also flexible molecules capable of forming hydrogen bonding networks both with other glycols and with functional groups within PU. Application of methodologies developed in **Chapter 4** (AIMD) or **Chapter 5** (TS generation incorporating conformational variability) would enable direct investigation of how glycol structure and hydrogen bonding behavior influence reactivity.

Another system of significant industrial interest is combined acidolysis-glycolysis, in which both acid and glycol reagents are used simultaneously. Despite its potential, the

mechanistic basis of this process remains poorly understood. AIMD simulations incorporating both reagents alongside a model reactive bond could help identify competitive interactions, cooperative effects, or conformational changes induced by mixed-reagent environments.

More broadly, many emerging PU chemical recycling strategies lack quantitative mechanistic understanding. The computational approaches developed and applied in this dissertation provide a flexible platform that can be extended to these systems, enabling systematic identification of structure-reactivity relationships and supporting the design of novel chemical recycling technologies.

A. Supporting Information for Differentiating Urethane and Urea Bond Activation in Polyurethane Foam Acidolysis

Materials

The model PUF sample was provided by The Dow Chemical Company and synthesized from VORANOL™ 8316 polyether polyol (the virgin polyol, 71 wt% of the model PUF) and VORANATE™ T-80 toluene diisocyanate (TDI). The exact formulation can be found in Table A.1. The model PUF used for this study was an open cell flexible foam. The Dow Chemical Company also provided Foam 2, Foam 3 and an EOL-PUF. The ratios of urethane and urea moles for Foam 2 and 3 can be found in A.9. The EOL-PUF is a mixture of mattress waste with an unknown composition collected from commercial waste in Europe.

Benzoic acid (99%), 3-fluorobenzoic acid (99%) and N-phenylurethane (98%) were purchased from Thermo Scientific Chemicals. 3-nitrobenzoic acid (99%), 2-fluorobenzoic acid (97%), methylbenzoic acid (98%), 4-methoxybenzoic acid (99%), pimelic acid (98%) and 1,3 diphenylurea (98%) were purchased from Sigma Aldrich. Hexadeuterated dimethyl sulfoxide (DMSO-d₆, 99.9%) was purchased from Cambridge Isotope Laboratories Inc. Industrial grade liquid nitrogen (N₂) was purchased from Airgas

Table A.1: Formulation used to prepare model PUF at an isocyanate index of 105.

Component	Type	Parts by Weight
VORANOL™ 8136 Polyol	Polyether Polyol	100
VORASURF™ DC 5987 Additive	Silicone Surfactant	0.8

Dabco 33 LV	Amine Catalyst	0.08
Niax Catalyst A-1	Amine Catalyst	0.03
Dabco T-9 Catalyst	Tin Catalyst	0.18
Water	Water	3.3
VORANATE™ T-80 Isocyanate	Toluene Diisocyanate (TDI)	42.7

Grinding Pre-treatment of Model PUF

Prior to the acidolysis reaction, model PUF was grinded into smaller particles. The foam chunks were first flask frozen in liquid nitrogen to increase their brittleness and transferred subsequently into a mechanical grinder equipped with cross blades. The foam was then dried in a desiccator for 24 hrs. After grinding, the particle size of model PUF was between 500 – 2000 μm .

PUF Acidolysis Kinetic Measurement Set-Up

Grinded model PUF and acid were added to a 25mL round bottom flask and stirred using a Fisher Scientific vortex mixer. Once stirred, the reaction flask was attached to a cold finger that was connected through Tygon tubing to a gas evolution burette (Figure A.1). A webcam was attached to the wall of the fume hood to record the volume in the gas evolution burette over time. EtOH was used to fill the burette during experiments for safety due to its low surface tension. The entire system was purged with Ar for 5-10 minutes to eliminate air

and moisture and 1 atm of Ar was left in the reaction system. After purging, the reaction flask was lowered into an oil bath at the desired temperature. The reaction mixture was stirred continuously using a magnetic stir bar at 400 rpm. Completion of reaction was determined by full homogenization of the reaction mixture and cessation of gas evolution. After reaction, the product mixture was cooled to room temperature. Videos of the gas evolution were processed in MATLAB R2019a.

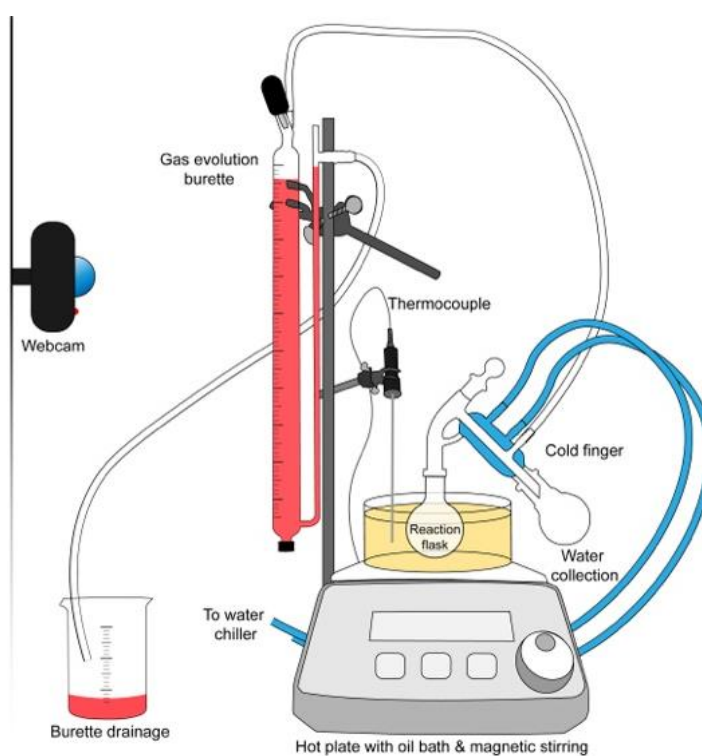


Figure A.1: Schematic of experimental setup for kinetic measurements. Reproduced with minor modifications from *ACS Sustainable Chemistry & Engineering* 11 (16), 6114-6128. Copyright 2024 American Chemical Society

Table A.2: Table of calculated moles, equivalents and mass percent of polyol and TDI fragments based on the foam formulation for the M-PUF used in this study.

Component	Mass (g)	Mw (g/mol)	Functionality	Moles	Equivalents	Mass %
polyol	100	3090	3	0.032	0.097	72.7
TDI	42.7	174.2	2	0.245	0.490	27.3
water	3.3	18	2	0.183	0.367	
added water	0.222	18	2	0.012	0.025	
TDI mass loss due to CO ₂	8.65					
Total	137.57				0.979	100.000

Table A.3: Table of relative moles of urethane and urea bonds in M-PUF based on 137.57 g of M-PUF from the above table.

	Total (moles)	TDI (moles)	Polyol (moles)	Moles / g PUF	CO ₂ (moles/g PUF)	CO ₂ (mL/g PUF)
Urethane	0.097	0.097	0.097	7.0E-04	7.0E-04	~16
Urea	0.197	0.393	0	1.4E-03	1.4E-03	~34
Moles of urethane + urea / g PUF	2.13E-03			2.13E-03		

Table A.4: Calculated molar ratio of acid to urethane and urea bonds based on the above calculated values and reaction scale.

Reaction Scale	0.5 g M-PUF	3.0 g BA
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Moles	1.065E-03 moles urethane + urea bonds	2.45E-02 moles BA
Molar Ratio	1 mole of urethane + urea bonds	23.06 moles BA

Table A.5: Example analysis methods and conclusions for BA experiments.

Analysis Method	Products Analyzed	Urethane Bonds?	Urea Bonds?	Conclusions
GPC	Polyol	✓	X	Polyol release is complete at 120 minutes.
Gas Evolution	CO ₂	✓	✓	CO ₂ release is complete at 300 minutes. Since urethane acidolysis is complete at 120 minutes, CO ₂ evolution continuing past this point has to be attributed to urea bond acidolysis.
¹ H NMR	Amide, urea oligomers	✓	✓	Amide signals continue to evolve until 300 minutes, signaling that acidolysis of both bonds are complete then. Urea oligomers are gone at 300 minutes, signaling that all urea bonds have been cleaved.

Table A.6: Reaction details for all acids tested.

Acid	Acid Loading (g)	PUF Loading (g)	PUF:Acid Mass Ratio	PUF:Acid Molar Ratio	Temperature (°C)
3-NBA	3	0.5	6:1	23:1	195
2-FBA	3	0.5	6:1	23:1	195
3-FBA	3	0.5	6:1	23:1	195
BA	3	0.5	6:1	23:1	195
4-MBA	3	0.5	6:1	23:1	195
4-MOBA	3	0.5	6:1	23:1	195
PiA	1.5	0.5	3:1	11.5:1	195

Table A.7: Calculated theoretical amounts of catalysts present in the M-PUF studied based on B.1 and amounts added to a BA acidolysis reaction.

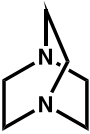
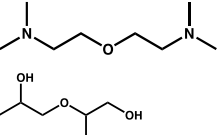
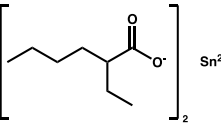
Name	Type	Structure	Calculated Amount (mg per 0.5 g M-PUF)	Amount used in reaction (mg per 0.5 g M-PUF)	Ratio Used
Dabco 33 LV	Amine Catalyst		0.29	0.58	2
Niax Catalyst A-1	Amine Catalyst		0.11	NA	NA
Dabco T-9 Catalyst	Tin Catalyst		0.65	1.3	2

Table A.8: ICP-OES results from two samples of M-PUF digested using HNO₃ and H₂O₂.

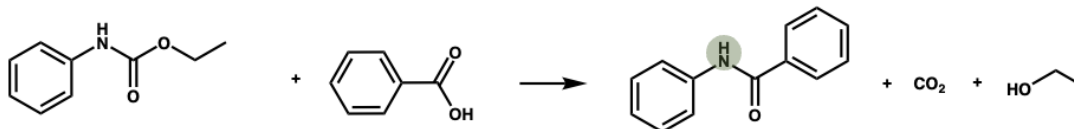
Sample (150 mg M-PUF)	Sn Line 1 (ppm)	Sn Line 2 (ppm)	Avg (ppm)	Percent of Theoretical (~1.5 ppm)
1	0.25	0.29	0.27	18%
2	0.85	0.82	0.84	56%

¹H Nuclear Magnetic Resonance

¹H NMR were run on products from the reactions to access the extent of the reaction and confirm the disappearance of oligomeric content. Reactions were run as described above. After the reaction mixture was cooled, the flask was removed from the ice bath, and 150 mg were taken from the flask without further separation or purification steps. The samples were dissolved in 600 μ L dimethyl sulfoxide (DMSO-d₆) and placed in a 5 mm glass NMR tube.

NMR measurements were performed with a Bruker Avance NEO 500 MHz spectrometer, which was equipped with a 5 mm X-nuclei optimized double resonance cryoprobe.

Model Urethane Reaction Scheme



Model Urea Reaction Scheme

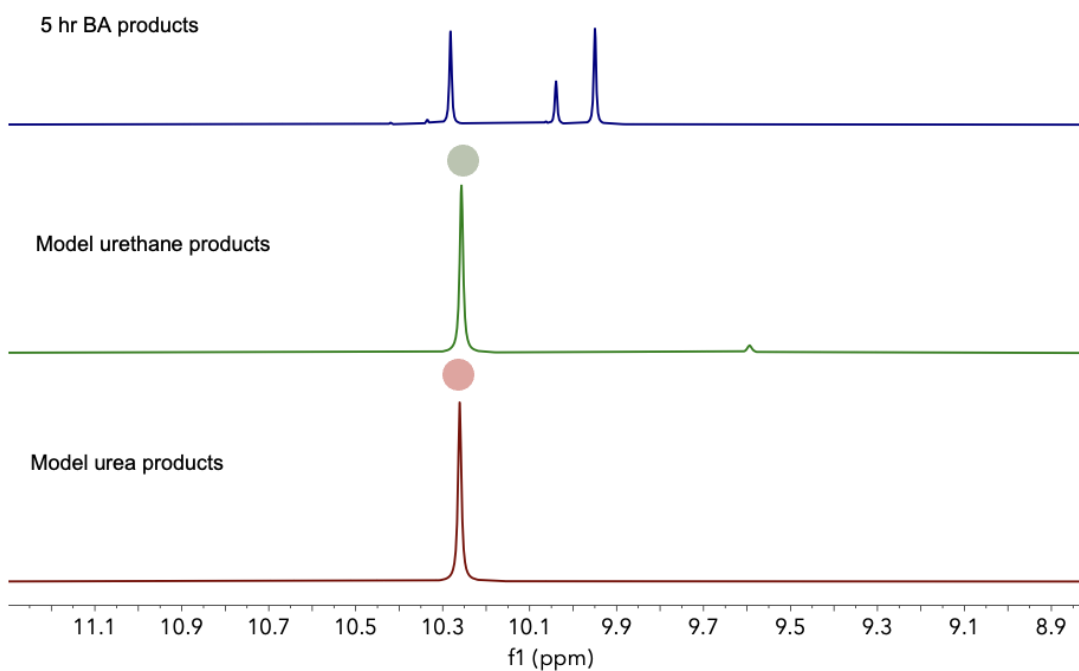
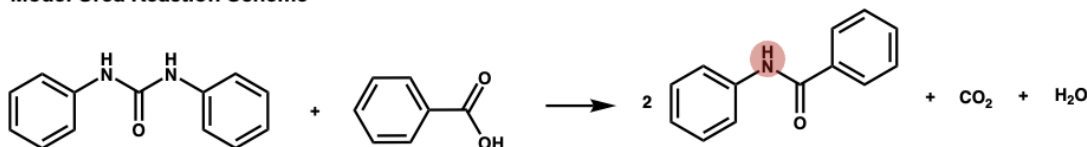


Figure A.2: Reaction schemes for acidolysis of model compounds, N-phenylurethane and 1,3 diphenylurea, with BA at 195°C, with the NH of the amide product highlighted. ^1H NMR spectrum of the amide region of the reaction mixture from acidolysis of M-PUF with BA at the end of reaction, 5 hours compared to the amide region of the model reaction products from acidolysis with BA. The small

peak at ~9.6 ppm in the model urethane product ^1H NMR is from the NH signal of unreacted model urethane.

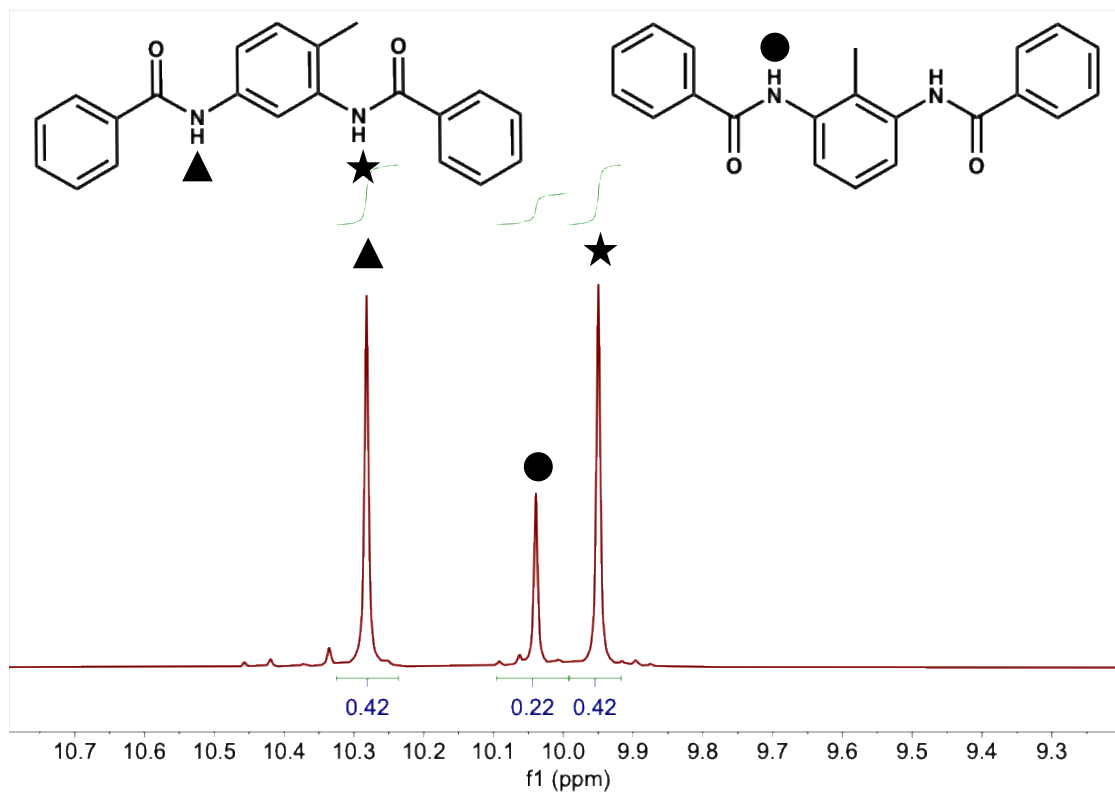


Figure A.3: ^1H NMR spectrum of the amide region of the reaction mixture from acidolysis of M-PUF with BA at 195 °C at the end of reaction, 5 hours. The two molecules represent the amide products from both urethane and urea acidolysis. As the foam was formulated with TDI which comes in the 2,4 and 2,6 isomers, with a relative ratio of 2:1, the above integrations match the ratio of these isomers.

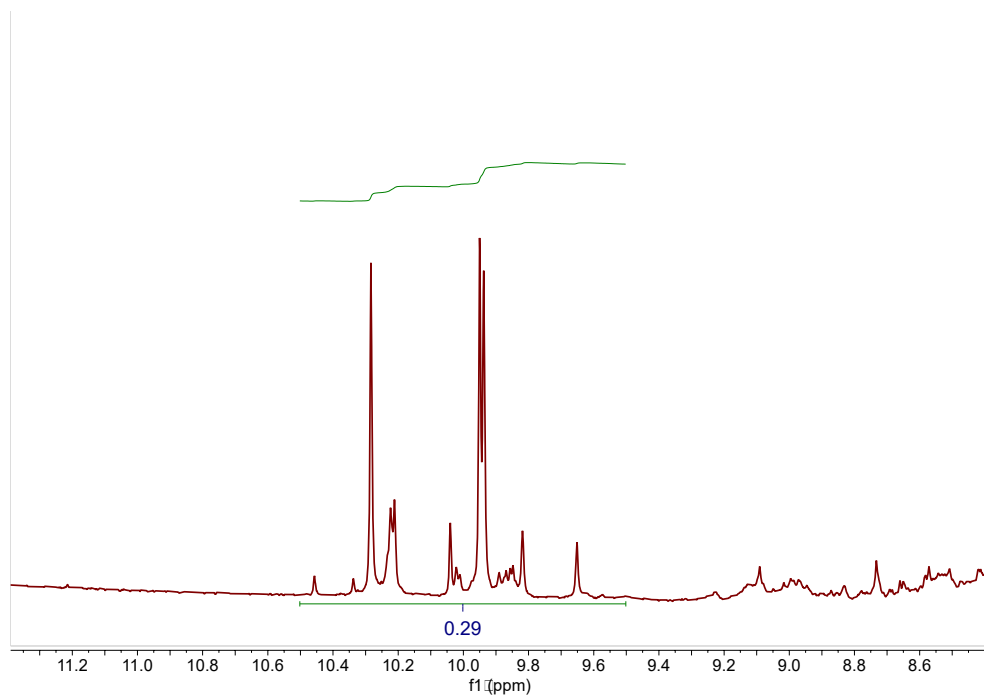


Figure A.4: ^1H NMR spectrum of the reaction mixture from acidolysis of M-PUF with BA at 195 °C, showing the integral of the amide region ($\delta^1\text{H} = 9.5 - 10.5$ ppm) at 2 hours.

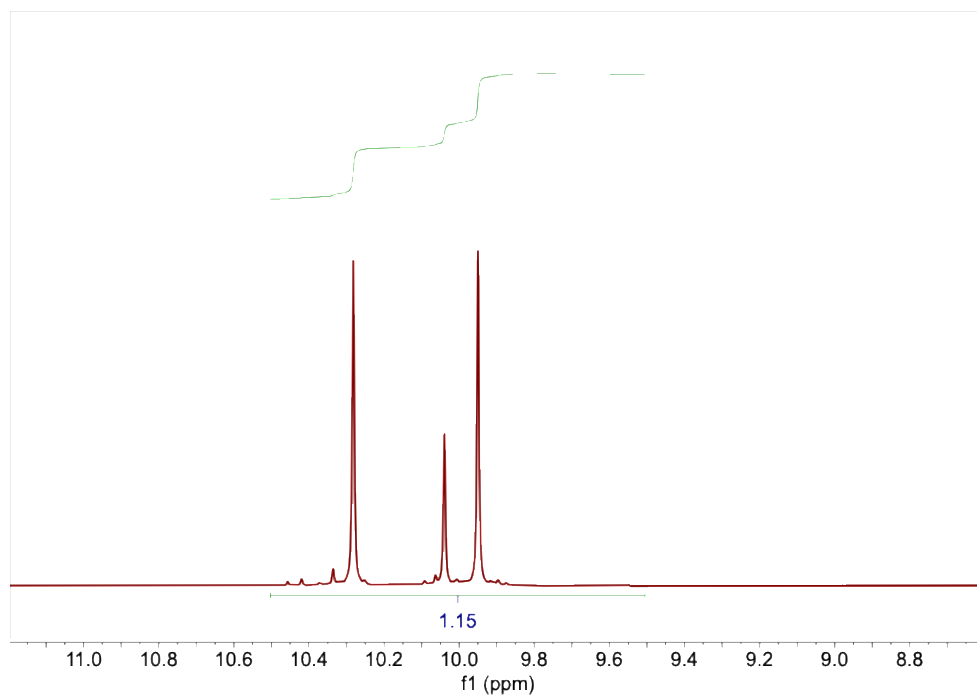


Figure A.5: ^1H NMR spectrum of the reaction mixture from acidolysis of M-PUF with BA at 195 °C, showing the integral of the amide region ($\delta^1\text{H} = 9.5 - 10.5$ ppm) at 5 hours. Compared to the integration above at 2 hours, we can see that the integration more than tripled indicating further amide formation.

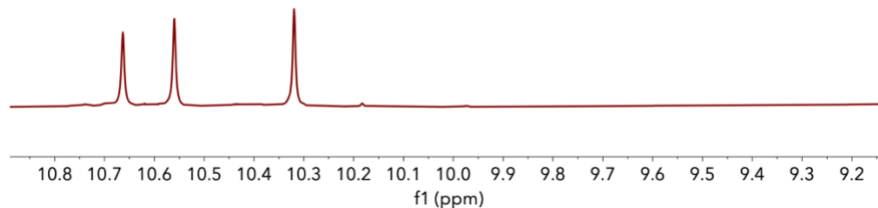


Figure A.6: ^1H NMR spectrum of the reaction mixture from acidolysis of M-PUF with 3-NBA at 195 °C at 1 hour (time at which CO_2 evolution ceased). Disappearance of the peaks to the right of the amide region, attributed to oligomeric urea content, indicate complete urea bond decomposition.

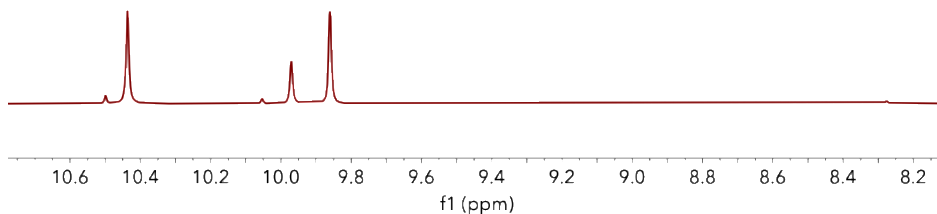


Figure A.7: ^1H NMR spectrum of the reaction mixture from acidolysis of M-PUF with 2-FBA at 195 °C at 1.7 hours (time at which CO_2 evolution ceased). Disappearance of the peaks to the right of the amide region, attributed to oligomeric urea content, indicate complete urea bond decomposition.

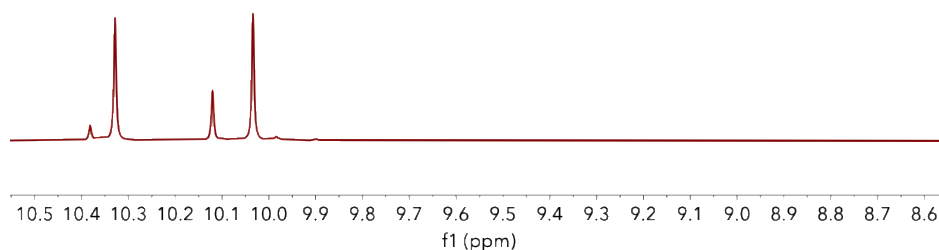


Figure A.8: ^1H NMR spectrum of the reaction mixture from acidolysis of M-PUF with 3-FBA at 195 °C at 2.7 hours (time at which CO_2 evolution ceased). Disappearance of the peaks to the right of the amide region, attributed to oligomeric urea content, indicate complete urea bond decomposition.

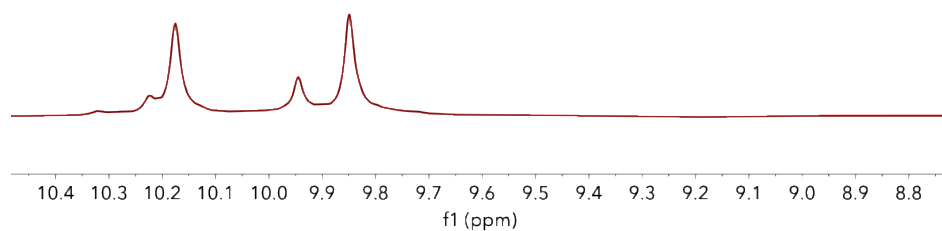


Figure A.9: ^1H NMR spectrum of the reaction mixture from acidolysis of M-PUF with 4-MBA at 195 °C at 7 hours (time at which CO_2 evolution ceased). Disappearance of the peaks to the right of the amide region, attributed to oligomeric urea content, indicate complete urea bond decomposition.

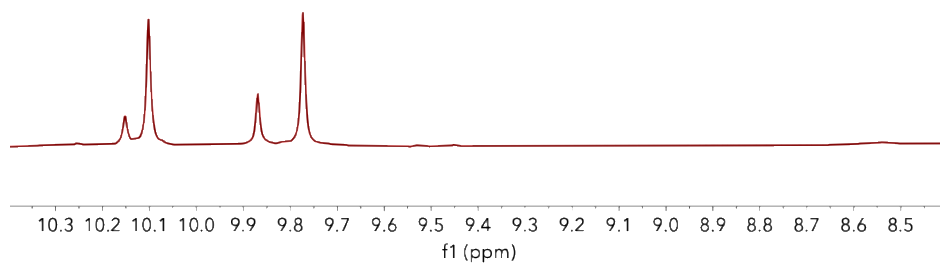


Figure A.10: ^1H NMR spectrum of the reaction mixture from acidolysis of M-PUF with 4-MOBA at 195 °C at 9 hour (time at which CO_2 evolution ceased). Disappearance of the peaks to the right of the amide region, attributed to oligomeric urea content, indicate complete urea bond decomposition.

Gel Permeation Chromatography

The GPC analyses were performed using a Waters Acquity APC system with three Acquity APC XT columns and an Acquity UPLC refractive index detector. The eluent used was THF and was pumped at a rate of 0.9 mL/min. For each sample, approximately 30 mg of the reaction mixture was dispersed in 3 mL of THF and was left standing for 24 hours to allow for the full solvation of the sample. The solutions were then filtered through a 0.45 μm PTFE membrane (Millipore) before injection. The injection volume to the columns was 25 μL , and the column was held at 35 °C. The results were calibrated using PEG/PEO standards. GPC was also performed on a reference sample of VORANOLTM 8136 Polyol to establish its molecular weight and distribution relative to the calibration used.

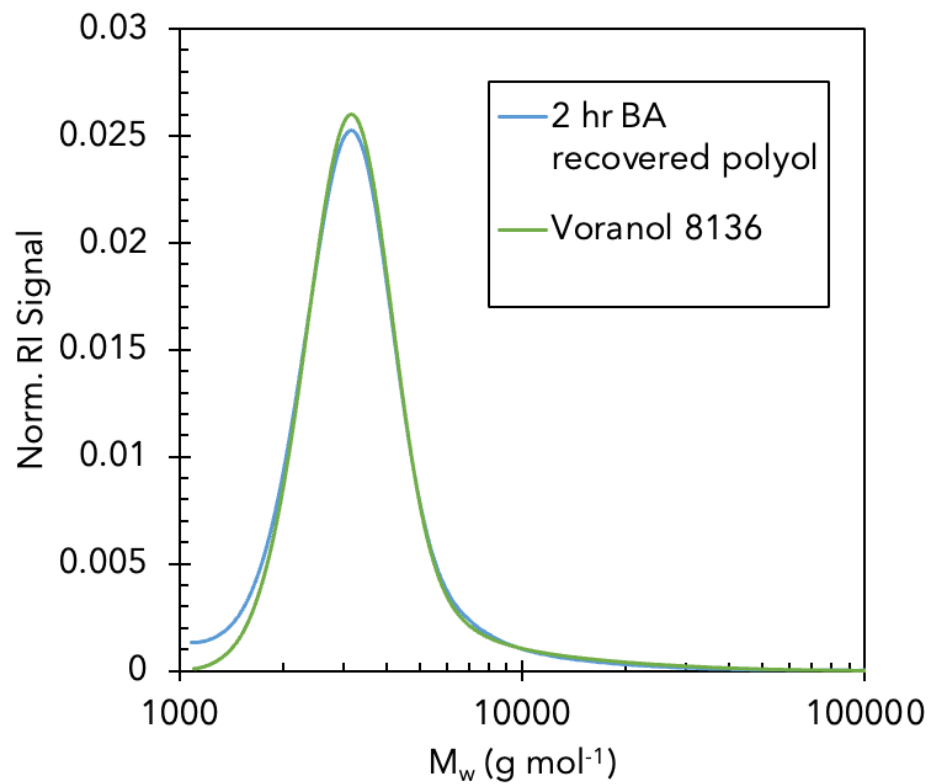


Figure A.11: Normalized GPC chromatograms of the recovered polyol from acidolysis with BA at 2 hours compared to the virgin VORANOL™ 8136 polyol used in the M-PUF formulation.

Gas Evolution

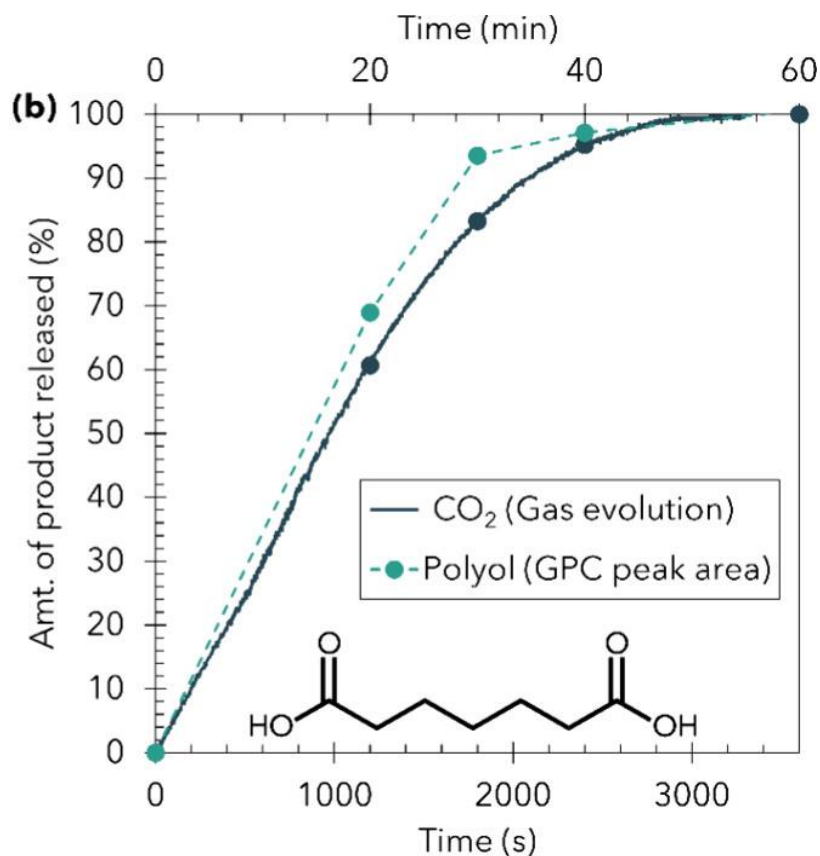


Figure A.12: Normalized percent of CO₂ (dark blue) and polyol (teal) released during acidolysis with PiA at 195 °C as a function of reaction time, measured by gas evolution and GPC, respectively. The fractional yields were calculated through normalization of the maximum amount of each product observed. The solid line is the experimental data associated with CO₂ release, and the dark blue data points are just shown for direct comparison to the GPC data. Reactions were executed with 0.5 g of M-PUF and 1.5 g of PiA under an inert (N₂) atmosphere. Reproduced with minor modifications from *JACS Au* 4 (8), 3194-3204. Copyright 2024 American Chemical Society

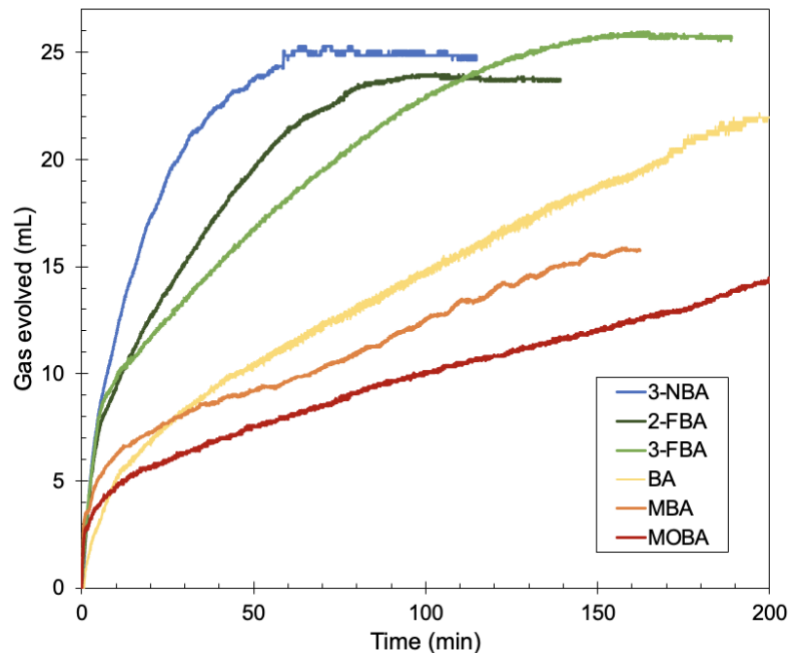


Figure A.13: CO₂ evolution during M-PUF acidolysis with 3-NBA, 2-FBA, 3-FBA, BA, 4-MBA and 4-MOBA at 195 °C showing two regimes. 3-NBA is the only acid without two distinct regimes, this is addressed in the discussion. Reactions were run with 3.0 g acid and 0.5 g M-PUF under inert atmosphere (Ar).

4-MBA and 4-MOBA have higher melting points compared to the other acids studied, 180 °C and 185 °C, respectively. Since these reactions were run at 195 °C, at very long reaction times (>2.5 hours) there was acid sublimation at the top of the round bottom flask above the oil bath. While this can be remedied by using a heat gun on the headspace (not on the reaction mixture itself) to continuously melt the acids back into reaction mixture, this influences the gas plot. As a result, at long times, samples from the reaction mixture can be used for further product analysis (GPC, NMR), but the gas evolution no longer reflects inherent reaction kinetics. To determine when urea decomposition is complete, the gas evolution from before acid sublimation is extrapolated out to the stoichiometric CO₂ release and the H-NMR spectra at this time is analyzed to ensure no urea oligomer content (Figure A.8 and A.9).

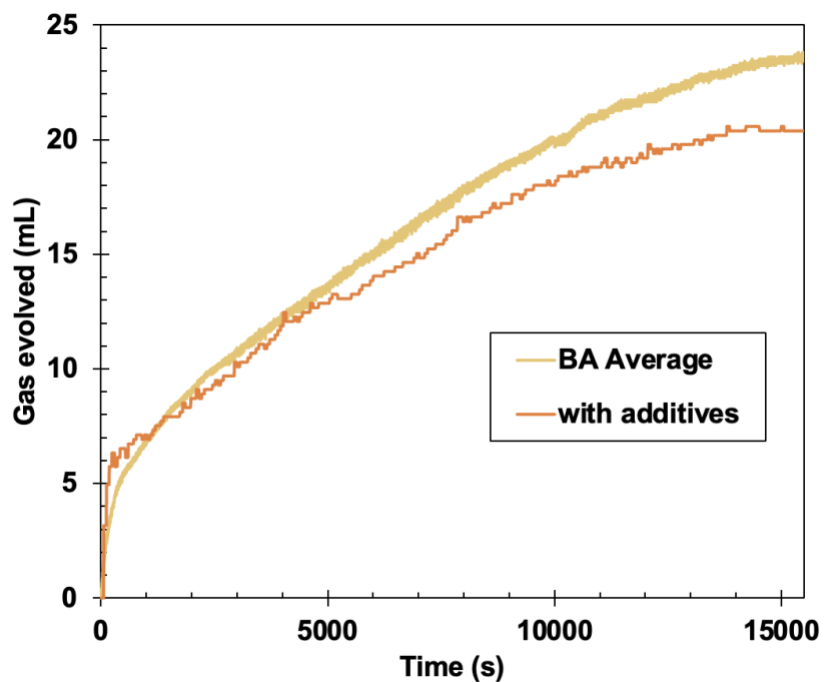


Figure A.14: Average gas evolution plot for BA acidolysis and BA acidolysis with added catalysts Dabco 33 LV and Dabco T-9. Reaction conditions: 0.5 g M-PUF, 3.0 g BA, 1 uL tin (II) octoate, 8 uL 1,4-Diazabicyclo[2.2.2]octane solution in water (0.58 mg), 195°C under an inert (Ar) atmosphere.

Table A.9: Table of mmol of urethane and urea bonds per gram of PUF for three different foam formulations.

	Foam	mmol urea/g PUF	mmol urethane/g PUF
	M-PUF	1.32	0.69
low H ₂ O	2	1.02	0.73
high H ₂ O	3	1.59	0.65

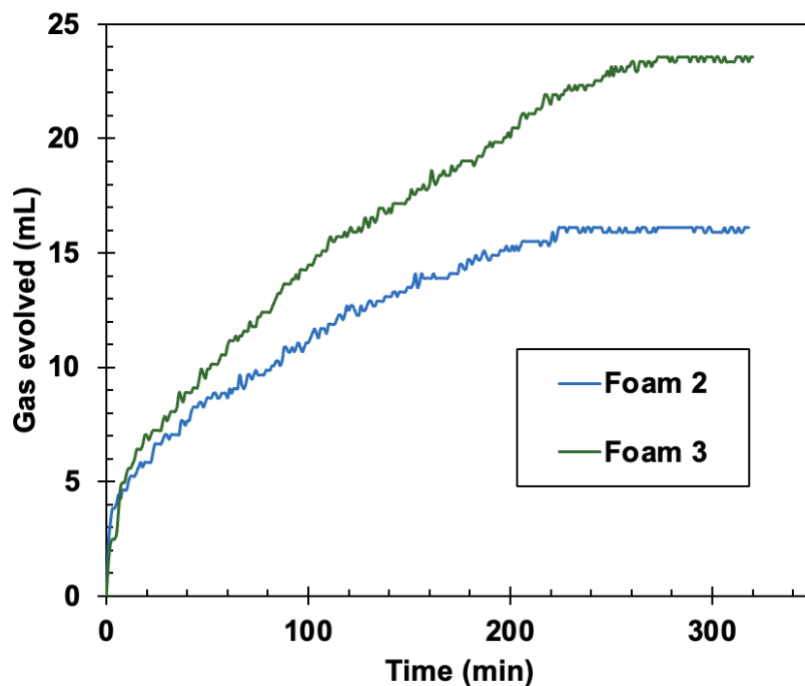


Figure A.15: Gas evolution plot for BA acidolysis with Foam 2 and Foam 3, both showing biphasic kinetics. Reaction conditions: 0.5 g F2/F3, 3.0 g BA, 195°C under an inert (Ar) atmosphere.

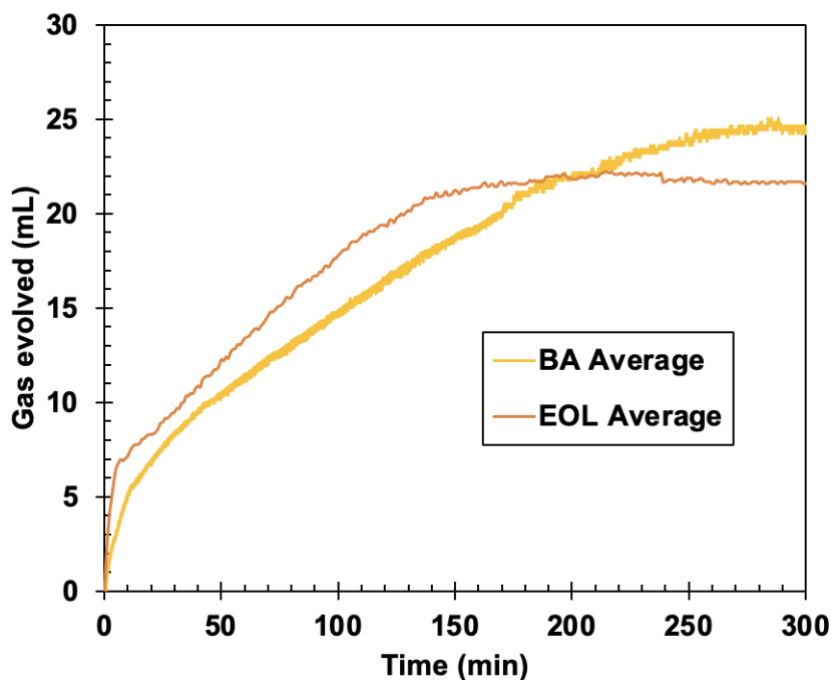


Figure A.16: Average gas evolution plot for BA acidolysis with M-PUF and end of life (EOL) PUF. Small differences can be attributed to the unknown composition of the EOL PUF. But, in general, these

results display the same biphasic behavior investigated in this paper. Reaction conditions: 0.5 g EOL PUF, 3.0 g BA, 195°C under an inert (Ar) atmosphere.

Gas Evolution Fitting

For each acid tested, at least three replicate trials were conducted at 195 °C to ensure repeatability of results. During the initial reaction period, several phenomena contribute to gas evolution: 1) thermal expansion of the Ar gas inside the round-bottom flask, and 2) the phase change of the acid from solid to liquid. To separate these effects from the gas generated by polyurethane acidolysis, control experiments were performed. These controls, repeated at least three times per acid, involved heating the acid and Ar (with no PUF) to 195°C while monitoring gas evolution. The control experiments yielded a consistent gas volume of approximately 11.8 mL across all acids and trials. To correct for these non-reactive contributions, we defined $t = 0$ for each acidolysis experiment as the time when 11.8 mL of gas had been created, and we subtracted this baseline value from all subsequent time points (i.e., the time at which $V = 11.8$ mL now corresponds to $V = 0$ mL and $t = 0$). Notably, the time to reach this baseline volume varied minimally between experiments. This induction-removed gas evolution data were fit to a constrained biexponential model of the form $V(t) = A_1(1 - e^{-k_1t}) + A_2(1 - e^{-k_2t})$ with the constraint $A_2 = 25 - A_1$ such that the total asymptotic gas volume satisfies $V(t \rightarrow \infty) = A_1 + A_2 = 25 \text{ mL}$, corresponding to the theoretical CO₂ volume produced from acidolysis of 0.5 g of PUF. The fits were performed using Python's `curve_fit` function (from `scipy.optimize`), with parameter bounds set to ensure physically meaningful values ($0 \leq A_1 \leq 25$ and positive rate constants $k_1, k_2 \geq 0$). Figure A.17 shows a graphical depiction of this fitting procedure. From this fit, rate constants and pre-exponential factors for both exponential regimes were extracted and included in Table A.10. Reported standard errors (SEs) include variability from

both experimental repeats and the fitting process. SEs are the same for A_1 and A_2 because A_2 is defined as $25 - A_1$ to impose the asymptotic behavior towards 25 mL of gas evolution. B.17 shows the induction-removed averaged data (solid line), experimental error ($\pm\sigma$, shaded area), and biexponential fits (dashed black line) for each acid.

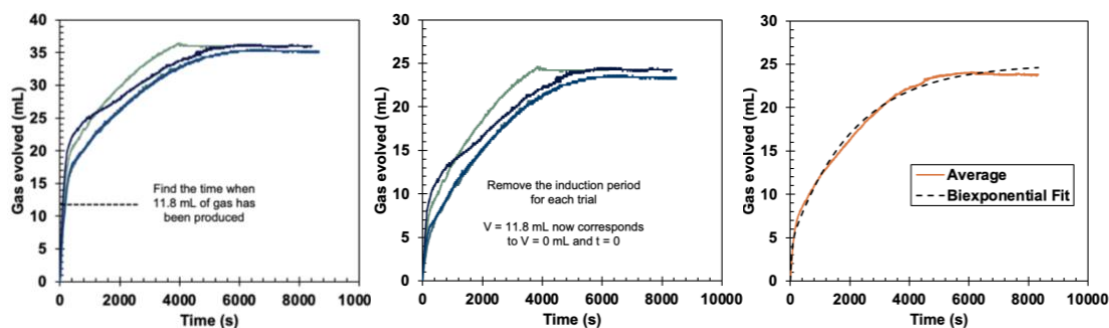


Figure A.17: Example of fitting procedure to extract kinetic parameters for acidolysis using 2-FBA.

Table A.10: Tabulated kinetic parameters and their standard errors for the second kinetic regime for acidolysis with monocarboxylic acids.

MCA	k_1 (min^{-1})		A_1 (mL)		k_2 (min^{-1})		A_2 (mL)	
	Value	SE	Value	SE	Value	SE	Value	SE
3-NBA	0.866	0.022	2.28	0.054	0.0558	2.3E-04	22.7	0.054
2-FBA	1.26	0.062	4.22	0.080	0.0286	9.7E-05	20.8	0.080
3-FBA	1.19	0.020	4.84	0.032	0.0224	5.4E-05	20.2	0.032
BA	0.723	0.007	3.77	0.022	0.0081	1.5E-05	21.2	0.022
4-MBA	0.878	0.016	6.33	0.022	0.0033	1.6E-05	18.7	0.022
4-MOBA	0.378	0.012	4.42	0.022	0.0031	7.6E-06	20.6	0.022

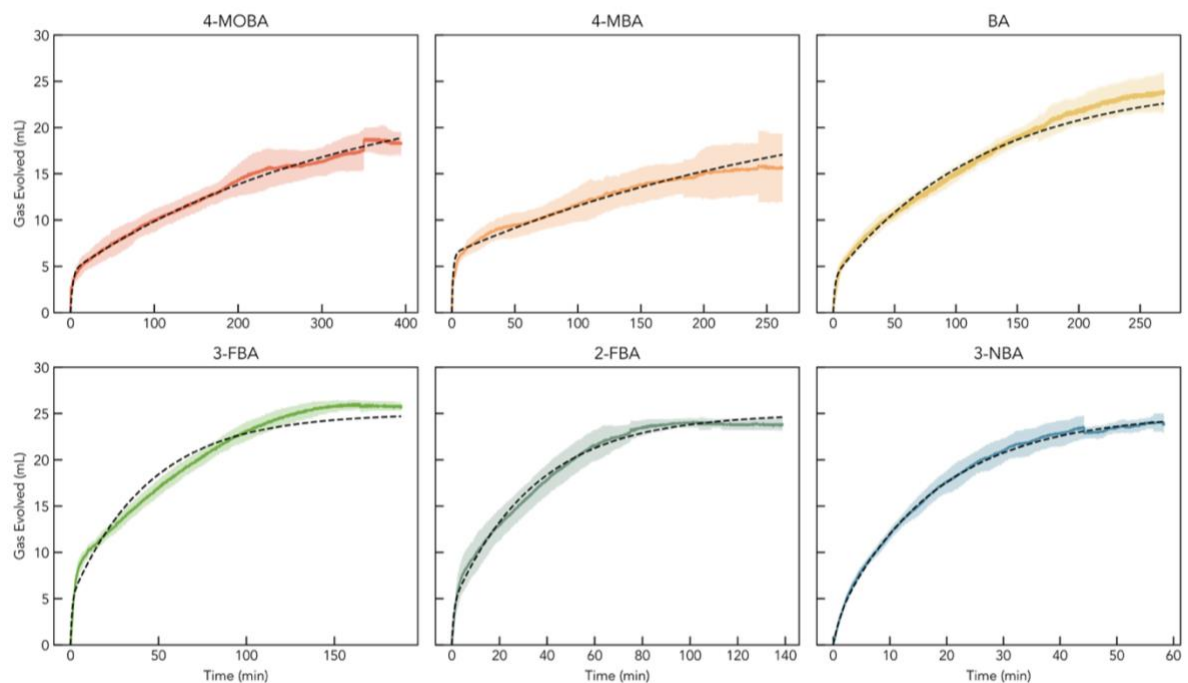


Figure A.18: Average CO₂ evolution during M-PUF acidolysis with 3-NBA, 2-FBA, 3-FBA, BA, 4-MBA and 4-MOBA at 195 °C (solid line) with experimental error from replicated (shaded area) and biexponential fits (dashed black line). Reactions were run with 3.0 g acid and 0.5 g M-PUF under inert atmosphere (Ar).

3-NBA discussion

3-NBA displays a near-single regime in gas evolution from acidolysis. However, we tested both a biexponential fit and a single first-order fit to compare. The biexponential fit better captures the gas evolution data from acidolysis with 3-NBA, showing that although the kinetics may visually appear to follow a single kinetic regime, there are still two distinct kinetic domains corresponding to urethane and urea. The first-order fit was performed using Python's `curve_fit` function (from `scipy.optimize`) for the constrained first-order rate law: $V(t) = 25 (1 - e^{-k_1 t})$. This function was constrained such that $V(t \rightarrow \infty) = 25 \text{ mL}$.

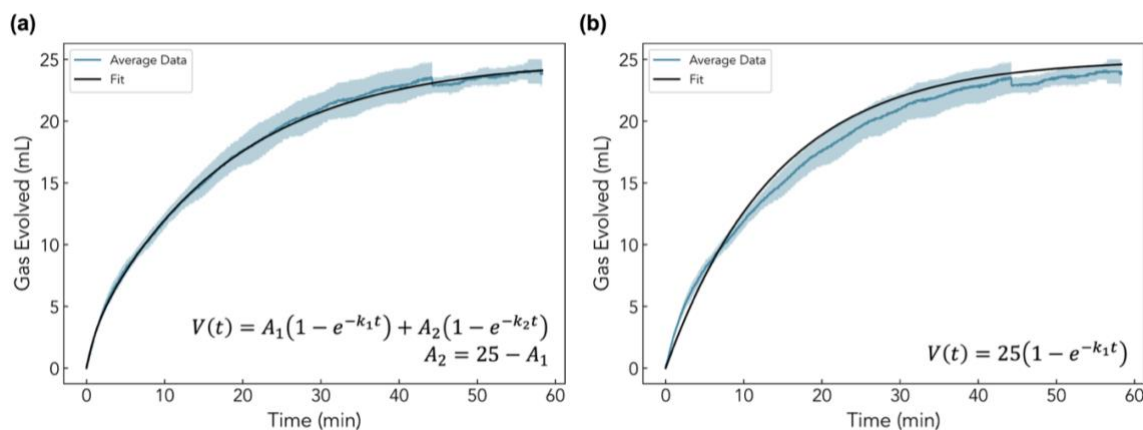


Figure A.19: Average CO₂ evolution during M-PUF acidolysis with 3-NBA at 195 °C (solid blue line) with experimental error from replicated (shaded area) and kinetic fits (black line, biexponential for **(a)** and single first-order for **(b)**). Reactions were run with 3.0 g acid and 0.5 g M-PUF under inert atmosphere (Ar).

Computational Analysis

Computational Methods. For the transition state analysis, DFT calculations were performed using Gaussian 16. Geometry optimizations and frequency analyses were conducted using the M06-2X functional with the cc-pVTZ basis set and D3 dispersion corrections, unless otherwise noted. Model systems for urea and urethane acidolysis are shown in Figure A.20.

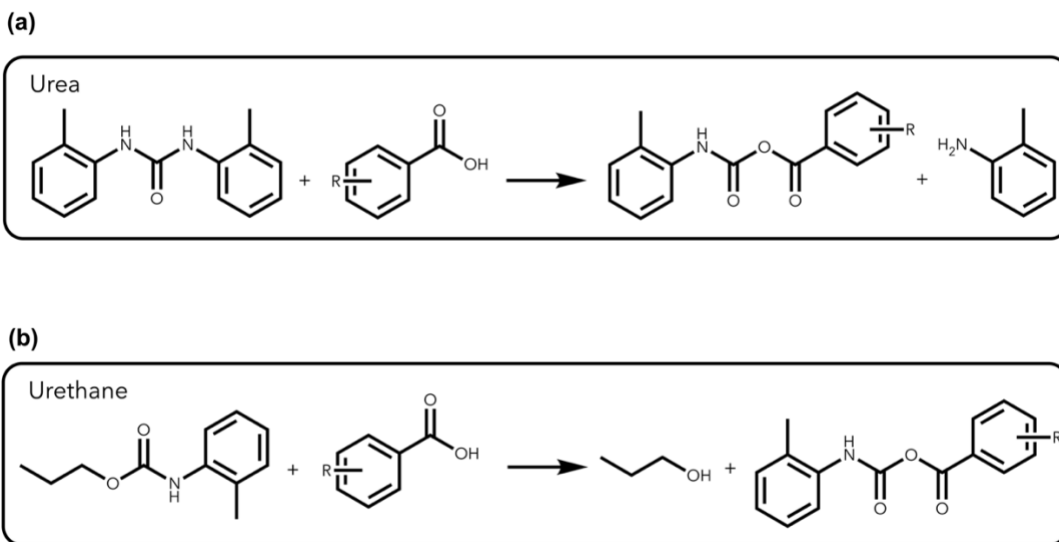


Figure A.20: Model reaction scheme for the acidolysis of urea **(a)** and urethane **(b)** using BA derivatives.

Transition states (TSs) for these reactions were located using the Berny algorithm implemented in Gaussian 16. Each TS structure was verified with a vibrational frequency analysis that confirmed the presence of a single imaginary frequency. Forward and reverse intrinsic reaction coordinate calculations were performed at the PBE0/cc-pVTZ level connecting each TS to the appropriate reactant and product complexes.

Barrier and Hammett Correlation. To evaluate the influence of acid electronics on reaction barriers, we calculated activation energies at M06-2X/cc-pVTZ level using: $E_A = \Delta H^\ddagger + RT$, where $\Delta H^\ddagger = \Delta H_{TS} - \Delta H_{reactants}$. The enthalpy values determined from DFT include the electronic energy, zero-point energy correction, and thermal corrections corresponding to a temperature of 448K. Entropic contributions to the rate area assumed to be captured by the experimental pre-exponential factor. Activation barriers were computed for BA and its electronic analogues to compare with experimental trends (Figure A.21(a) and (b)).

The calculated barriers for urethane acidolysis were invariant across the acid set, consistent with the observed experimental insensitivity to acid electronics. In contrast, urea acidolysis barriers decreased with more electron-withdrawing acids, mirroring the trend observed in the experimental Hammett plot.

We then converted these DFT-calculated activation energies to $\text{Log}(k/k_{BA})$, assuming that the pre-exponential factor does not vary between acids. With this assumption, we can derive the equation $\ln(k/k_{BA}) = E_{A,BA}/RT - E_A/RT$. The results of this analysis corroborate the experimental trends, including a ρ of 2.1 for urea and no strong dependence on electronics for urethane acidolysis (Figure A.21(c) and (d)).

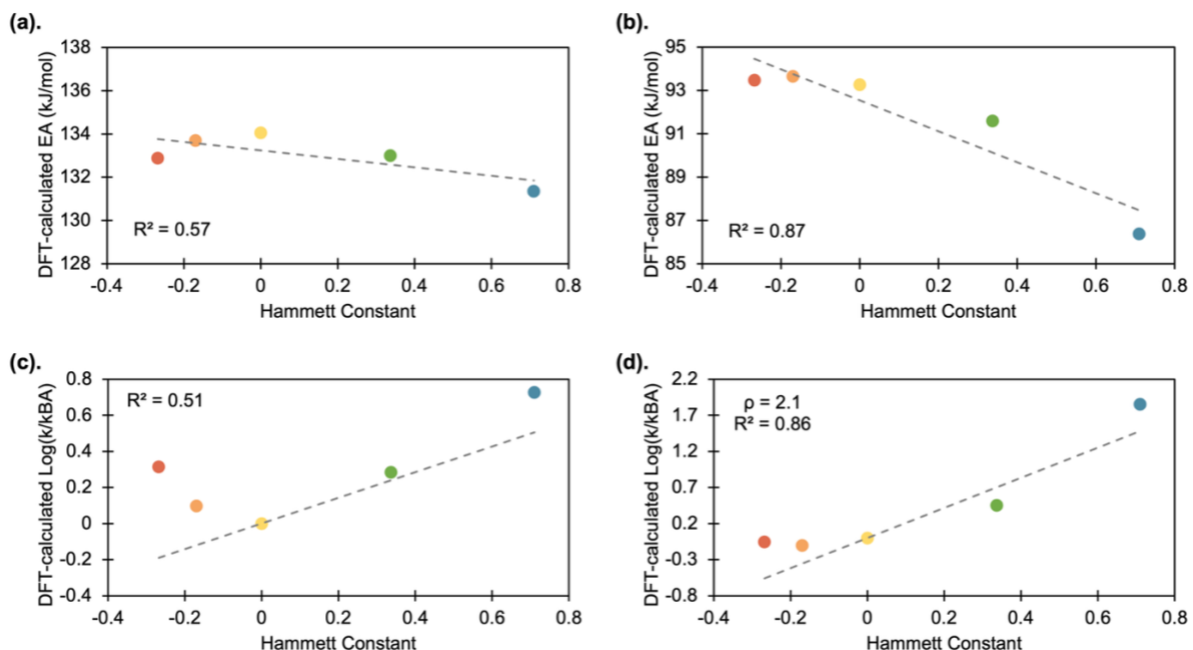


Figure A.21: DFT-calculated barriers for urethane **(a)** and urea **(b)** acidolysis reactions vs the Hammett constant of the MCA used in the reaction. Dashed lines represent linear fits. DFT-calculated Log(k/kBA) for urethane **(c)** and urea **(d)** acidolysis reactions vs the Hammett constant of the MCA used in the reaction. Dashed lines represent linear fits, constrained to go through the origin, with the slope (ρ) indicated.

Although these computational trends are consistent with experimental observations, the absolute barriers deviate from our expectations. Specifically, DFT predicts larger barriers for urethane acidolysis than for urea, contrary to experimental observations where urethane acidolysis is faster. This discrepancy arises from the simplified model urethane system. In the experimental system, the urethane system involves a large polymeric polyol group. To account for this, we systematically increased the complexity of our model urethane system. As shown in A.22, increasing the polyol tail complexity leads to a consistent decrease in the ΔH of the reaction which is directly related to a reduction in the E_A .

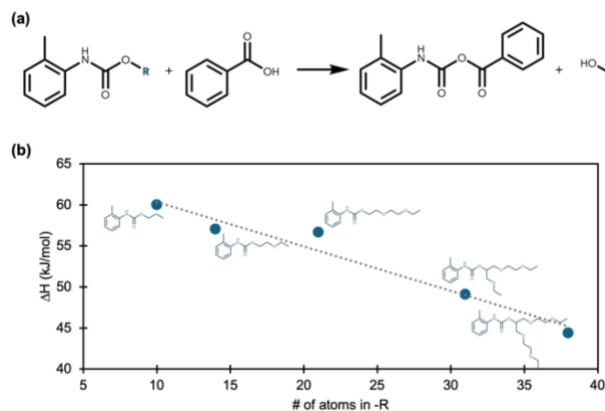


Figure A.22: (a) Model urethane reaction scheme with polyol tail represented by R. (b) ΔH of urethane acidolysis reaction vs the number of atoms in the polyol tail (R).

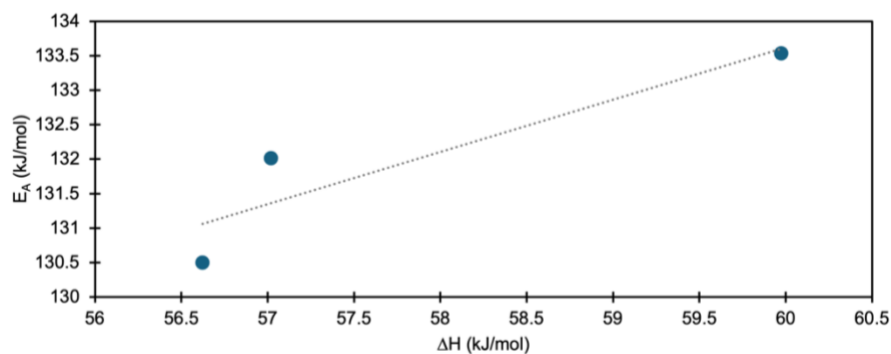


Figure A.23: DFT-calculated E_A vs ΔH for urethane acidolysis reaction with varied polyol tail. A direct relationship is observed between E_A and ΔH .

Bond Length Comparison. To make a structural and chemical argument for the electronic sensitivity effects observed both computationally and experimentally, the bond lengths in the urea and urethane transition states were compared. Table A.11 and A.12 show these bond lengths for urea and urethane transition states, respectively.

Table A.11: Urea acidolysis TS key bond lengths

Acid	C6-N5 (Å)	O3-H4 (Å)
------	-----------	-----------

3-NBA	1.736	2.000
2-FBA	1.710	1.943
3-FBA	1.713	1.957
BA	1.701	1.930
4-MBA	1.695	1.916
4-MoBA	1.688	1.900

Table A.12: Urethane acidolysis TS key bond lengths

Acid	C6-O5 (Å)	O3-H4 (Å)
3-NBA	1.690	1.386
2-FBA	1.710	1.405
3-FBA	1.677	1.356
BA	1.697	1.387
4-MBA	1.691	1.377
4-MoBA	1.685	1.366

Table A.13: Sum of electronic and thermal energies (E), enthalpies (H), and Gibbs free energies (G) in Hartrees and imaginary frequencies in cm^{-1} , where applicable, for all reactant and transition state structures for acidolysis with MCAs. Theory: M06-2x, cc-pVTZ, GD3, T=448K

Structure	E (Hartrees)	H (Hartrees)	G (Hartrees)	Imag. Freq. (cm^{-1})
Rep. urethane	-633.128361	-633.126942	-633.232753	-
Rep. urea	-765.635284	-765.633866	-765.751077	-
3-NBA	-625.181749	-625.18033	-625.263488	-
3-NBA Ureth TS	-1258.260081	-1258.258662	-1258.416387	436.55
3-NBA Urea TS	-1390.782717	-1390.782717	-1390.838486	274.87
2-FBA	-519.932421	-519.931002	-520.006126	-
2-FBA Ureth TS	-1153.010000	-1153.008581	-1153.157415	419.13
2-FBA Urea TS	-1285.532876	-1285.531457	-1285.690743	248.13
3-FBA	-519.938541	-519.937122	-520.011225	-
3-FBA Ureth TS	-1153.016246	-1153.014827	-1153.163289	470.29
3-FBA Urea TS	-1285.538942	-1285.537523	-1285.696536	250.70
BA	-420.682403	-420.680984	-420.751246	-
BA Ureth TS	-1053.759704	-1053.758285	-1053.902759	428.73
BA Urea TS	-1186.282164	-1186.280745	-1186.436065	240.61
4-MBA	-459.962930	-459.961511	-460.040781	-
4-MBA Ureth TS	-1093.040369	-1093.03895	-1093.192886	433.32
4-MBA Urea TS	-1225.562543	-1225.561124	-1225.725714	235.90
4-MOBA	-535.170940	-535.169521	-535.251345	-
4-MOBA Ureth TS	-1168.248686	-1168.247268	-1168.402746	443.88
4-MOBA Urea TS	-1300.770623	-1300.769204	-1300.935964	229.51

B. Supporting Information for Assessing the Conformational Landscape of Dicarboxylic Acids Using Ab Initio Molecular Dynamics: The Role of Phase and Intermolecular Interactions

Computational Methods

Methods

Both AIMD and direct energy minimization calculations were performed with Vienna Ab initio Simulation Package (VASP). Table B.1 lists the number of molecules, box size, and density for each of the simulations performed. The direct energy minimization calculations were all performed at the 1 molecule simulation while the AIMD simulations were performed with varying numbers of molecules to ensure that finite size effects were overcome (Fig. B.2). The effect of initial configuration was investigated with succinic acid (SA) and determined to not have an impact on the final conformer distribution as seen in Fig. B.3. As a result, all AIMD calculations in this paper were initialized with a mix of two different representative conformers, as shown in Fig. B.4, unless otherwise noted. To analyze the calculation, only data after equilibration (35 fs) was considered (Fig. B.5). Equilibration was determined by monitoring the average moment of inertia over time and was standardized for all acids and simulations. In the production period, the probability of forming internal and external hydrogen bonds was calculated where applicable using the process depicted in Fig. B.6 and B.7. When comparing direct energy minimization and AIMD results, we kept all possible parameters constant. The main theoretical difference between these simulations, other than the dynamics, was the influence of thermal fluctuations. While the AIMD calculations were performed in the canonical ensemble with the Andersen thermostat, the direct energy minimization calculations

were run at 0K. However, we confirmed that this should not induce large structural differences by varying the temperature in the AIMD simulations and analyzing the results in Fig. B.8. Finally, we provide example input files for our direct energy minimization and AIMD calculations in Fig. B.9, B.10, and B.11.

Table B.1. Number of molecules, box size, and density for AIMD calculations

Acid	# of molecules	Box side length (Å)	Density (g/cm³)
MA	1	20	0.024
	8	10.9	1.2
	12	12.4	1.2
	16	13.7	1.2
FA	1	20	0.024
	8	10.9	1.2
	12	12.4	1.2
	16	13.7	1.2
SA	1	20	0.025
	8	10.9	1.2
	12	12.5	1.2
	16	13.8	1.2

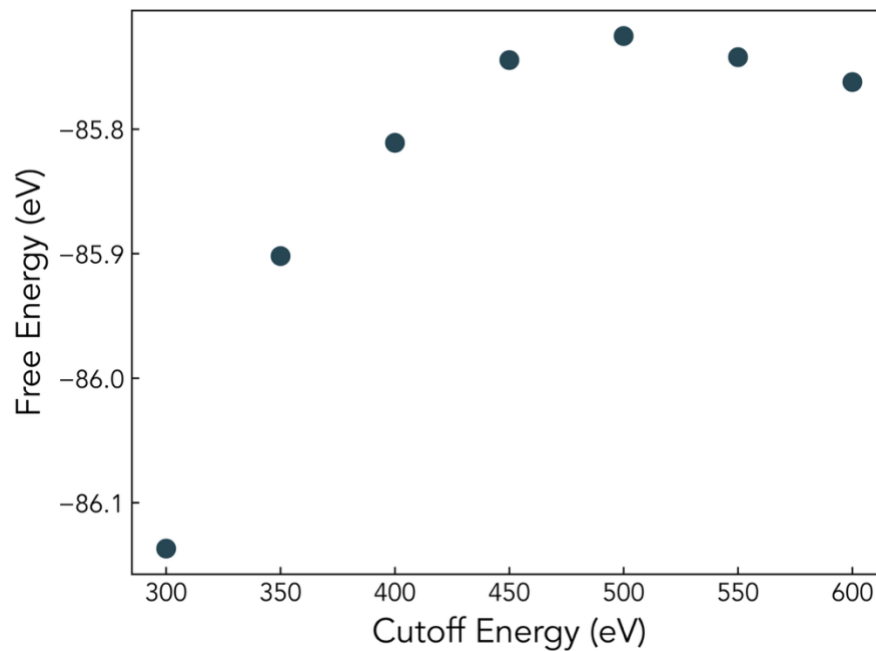


Figure B.1. Cutoff energy convergence for 1 SA molecule in a $20 \times 20 \times 20 \text{ \AA}^3$ simulation box. VASP, PBE functional with PAW correction.

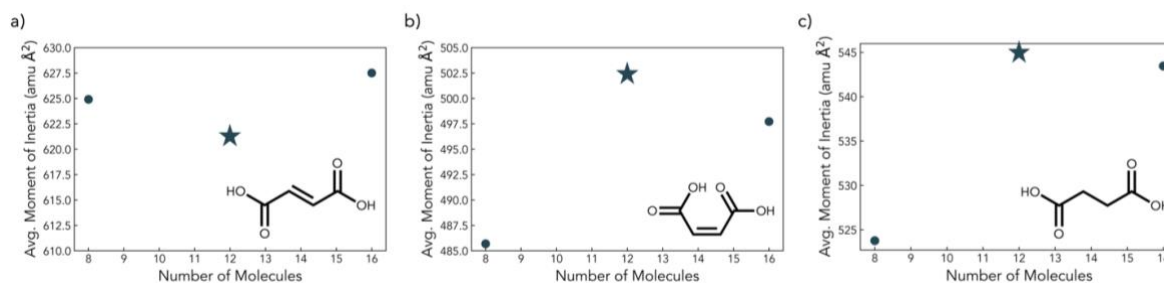


Figure B.2. Average moment of inertia (I) from production period of AIMD calculations with varying number of acid molecules and a density of 1.2 g/cm^3 for FA (a), MA (b), and SA (c).

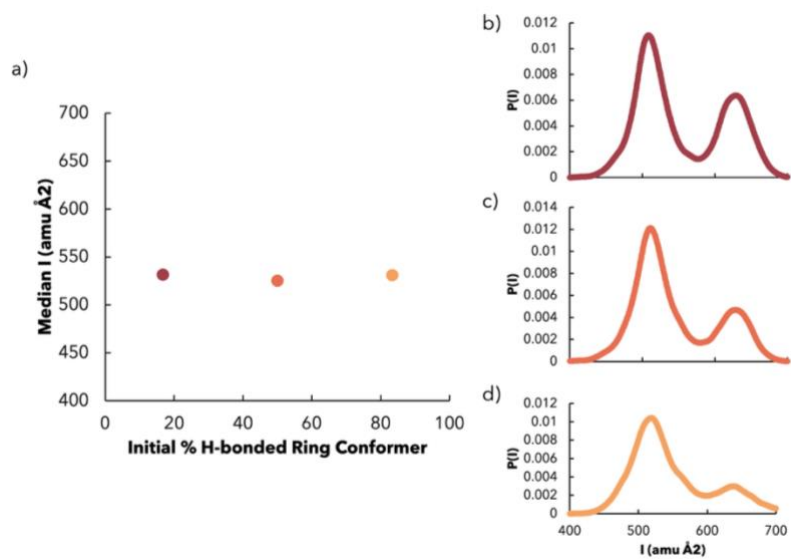


Figure B.3. a) Median I at equilibrium for AIMD simulations with 12 SA molecules of varying initial conformer distributions. b) I distribution of 2 hydrogen-bonded rings and 10 chains. c) I distribution of 6 hydrogen-bonded rings and 6 chains. d) I distribution of 10 hydrogen-bonded rings and 2 chains.

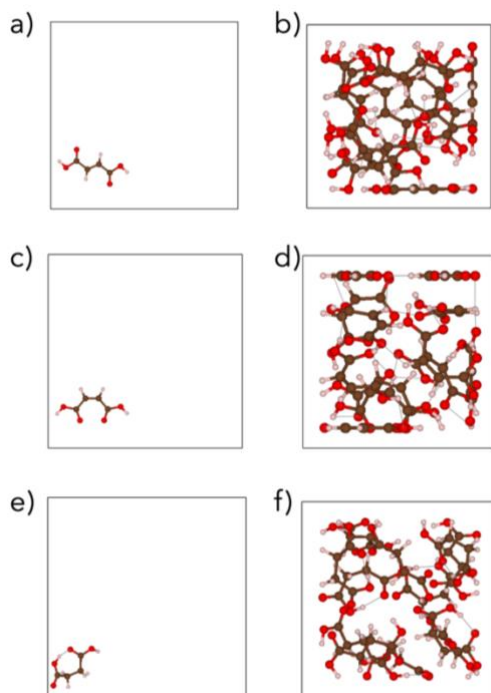


Figure B.4. Initial configurations for AIMD calculations – a) FA vapor (chain), b) FA condensed (50% chain 1, 50% chain 2), c) MA vapor (non-H bonded ring), d) MA condensed (50% H bonded ring, 50% non-H bonded ring), e) SA vapor (H bonded ring), and f) SA condensed (50% H bonded ring, 50% chain).

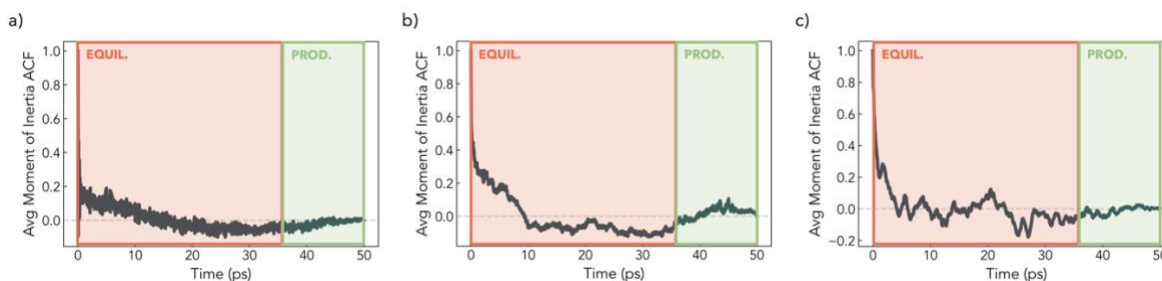


Figure B.5: Moment of inertia (I) autocorrelation function (ACF) for FA (a), MA (b), and SA (c) with the equilibration period shown in red and the production period shown in green. VASP, PBE functional with PAW correction, 12 molecule simulations, 1.2 g/cm³ density, 1 fs time step, canonical ensemble, Andersen thermostat.

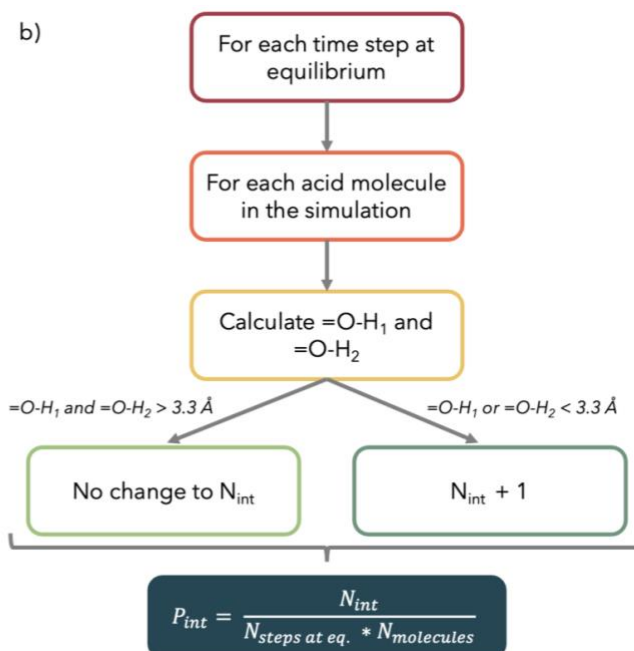
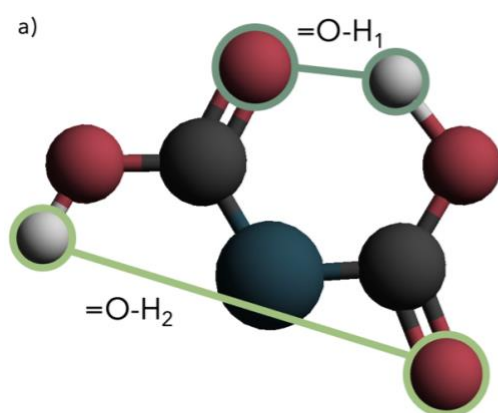


Figure B.6. a) Scheme of generic DCA molecule with bond distances considered in internal hydrogen bonding calculations. b) Calculation workflow for the internal hydrogen bonding probability, P_{int} , calculation.

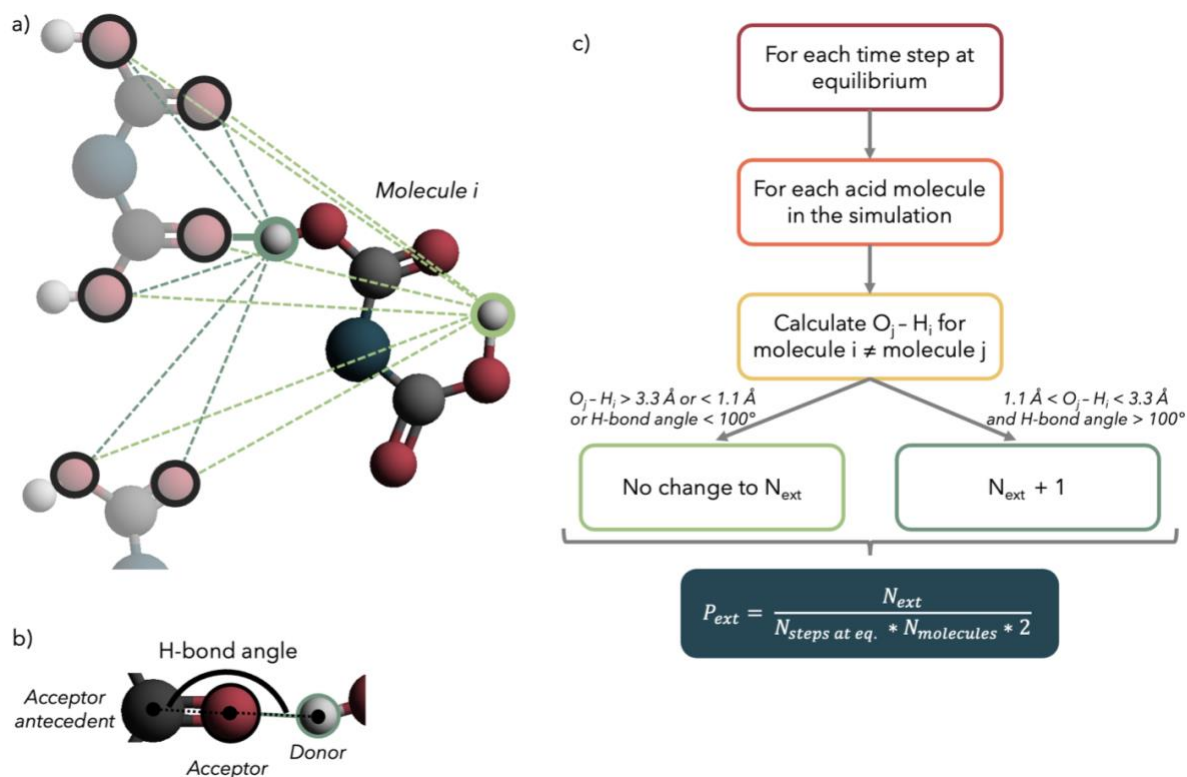


Figure B.7. a) Scheme of generic DCA molecule, i , with example of bond distances considered in external hydrogen bonding calculations. b) Example hydrogen bond angle calculation, using acceptor antecedent – acceptor – donor angle. c) Calculation workflow for the external hydrogen bonding probability, P_{ext} , calculation.

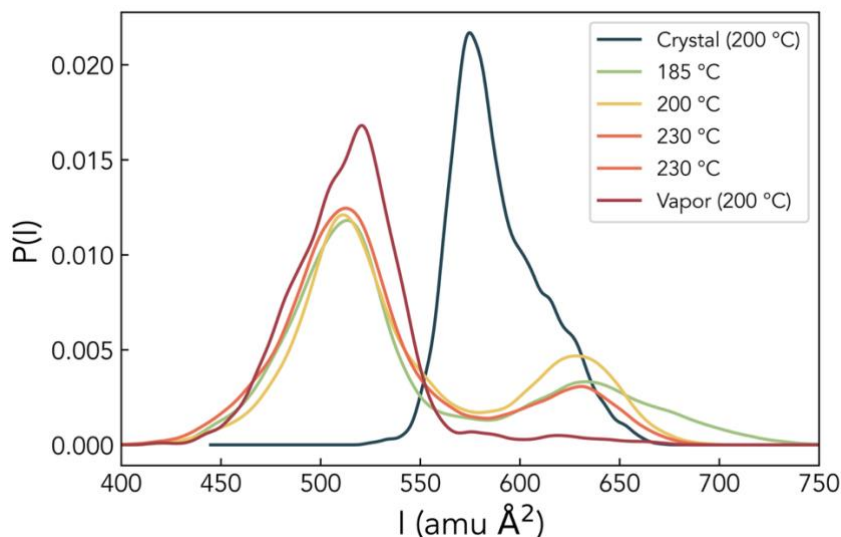


Figure B.8. Moment of inertia distribution for AIMD simulations of varying temperatures with 12 SA molecules. Density for 185 – 230 °C = 1.2 g/cm³. Density for vapor phase = 0.025 g/cm³ and for crystal phase = 1.62 g/cm³.

```
# Example direct energy
minimization calculation
# =====

# General Setup
SYSTEM = DCA molecule in a box      ! System name for tracking
PREC = NORMAL                       ! Precision setting for calc.
ENCUT = 500                         ! Energy cutoff for plane-wave basis set (eV)
ALGO = Fast                         ! Algorithm choice for electronic min.
LREAL = Auto                        ! Automatic projection in real space
ISMEAR = 0                          ! Gaussian smearing
ISYM = 0                            ! Symmetry turned off to allow full relaxation
NCORE = 1                           ! Number of cores used for parallelization

# Geometry Optimization Settings
IBRION = 2                          ! Conjugate gradient algorithm
NSW = 100                           ! Maximum number of ionic steps
IVDW = 2                            ! Van der Waals correction (TS method)
EDIFFG = -0.02                       ! Force convergence criteria (eV/Å)
EDIFF = 1E-6                        ! Energy convergence criteria (eV)
```

Figure B.9. Example INCAR file for direct energy minimization calculations

```

# Example AIMD simulation
# =====

# General Setup
SYSTEM = DCA molecules in a box      ! System name for tracking
PREC = NORMAL                        ! Precision setting for calc.
ENCUT = 500                          ! Energy cutoff for plane-wave basis set (eV)
ALGO = Fast                          ! Algorithm choice for electronic min.
LREAL = Auto                         ! Automatic projection in real space
ISMEAR = 0                           ! Gaussian smearing
ISYM = 0                             ! Symmetry turned off to allow full relaxation
NCORE = 1                            ! Number of cores used for parallelization

# Molecular Dynamics Settings
IBRION = 0                           ! Ab initio molecular dynamics (AIMD) calc
NSW = 50000                          ! Total number of MD time steps
POTIM = 1                            ! Time step for MD (fs)
IVDW = 2                             ! Van der Waals correction (TS method)
ISIF = 2                             ! Canonical ensemble (constant NVT)
MDALGO = 2                           ! Andersen thermostat
TEBEG = 473; TEEND = 473             ! Initial and final temperatures for MD (K)

```

Figure B.10. Example INCAR file for vapor and condensed phase AIMD simulations

```

Gamma-point only
0
Monkhorst Pack
1 1 1
0 0 0

```

Figure B.11. Example KPOINTS file for AIMD and direct energy minimization calculations

Proton hopping in AIMD simulations

As noted in the paper, we observed proton hopping during AIMD simulations (as seen in Fig. B.12). This can be seen in the results for fumaric acid (FA), where a non-zero P_{int} is reported although it is physically impossible for FA to form an intramolecular hydrogen bond without undergoing isomerization. Importantly, the influence of these rare events is largely filtered out in our analysis. Our Gaussian fits of these distributions do not capture this shoulder

and molecules undergoing proton hopping were also not captured by our random snapshots. Additionally, our hydrogen bonding calculations do capture proton hopping interactions, which is simply another form of intermolecular interactions. Thus, our structural and hydrogen bonding conclusions remain unaffected by these transient events.

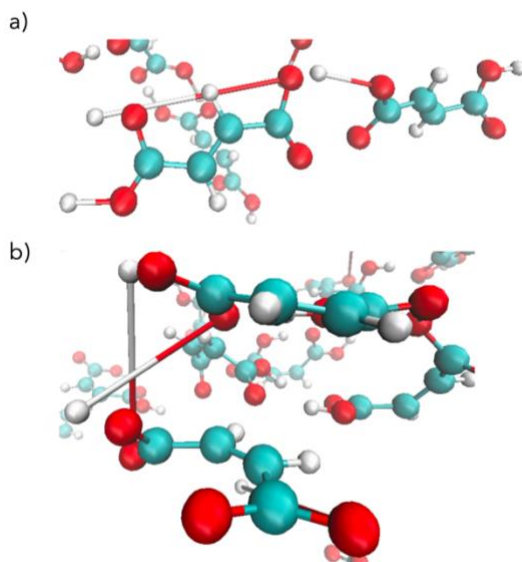


Figure B.12. Proton hopping in FA (a) and MA (b) simulations

Thermostat variations

To test the robustness of our conclusions with different thermostats, we compared the results of the SA condensed phase simulation with the Andersen and Nose-Hoover thermostats. Table B.2 compares the key observables obtained from these simulations.

Table B.2. Key observables for SA condensed phase simulations run with Andersen and Nose-Hoover thermostats.

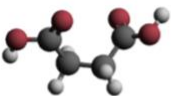
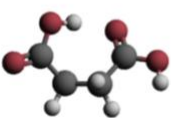
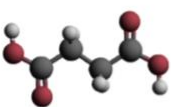
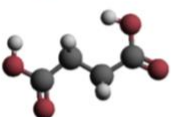
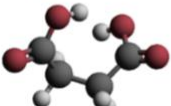
Value	Andersen Value	Nose-Hoover Value
Curve 1 Mean	509	508
Curve 2 Mean	629	608
Curve 1 St Dev	25	28
Curve 2 St Dev	25	41
Area Curve 1	0.7	0.7
Area Curve 2	0.3	0.3
P_{int}	0.4	0.5
P_{ext}	0.8	0.6

The largest observed differences were in the standard deviation (σ) of the high-I conformer distribution and the hydrogen bonding probabilities. Importantly, these variations do not affect our overall conclusions. The broader distribution under the Nose-Hoover thermostat is likely due to the continuous coupling of the simulation to the heat bath that facilitates the sampling of a wider range of thermal fluctuations. Additionally, while the P_{int} and P_{ext} values vary slightly, both thermostats yield similar populations of ring-like and chain-like conformers ($P_{\text{int}} = 0.4\text{-}0.5$) and comparable intermolecular hydrogen bonding networks ($P_{\text{ext}} = 0.6\text{-}0.8$). More importantly, both thermostats show the presence of the chain-like conformer peak, which would not be predicted with direct energy minimization alone. These results confirm that our conclusions are robust with respect to thermostat choice.

Representative Conformers

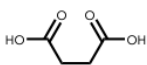
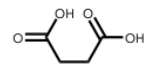
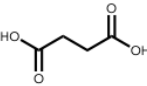
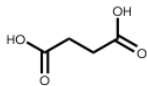
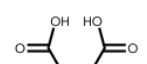
To give more structural details about the representative conformers of SA, we calculated the molecular planarity parameter (MPP) and the span of deviation from plane (SDP) per the protocol outlined by Lu et al.¹⁵¹ Larger values of MPP and SDP correspond to less planar molecules. From this analysis, we show that the ring conformers of SA are not planar.

Table B.3. Representative conformers of SA identified through direct energy minimization with DFT, with calculated moments of inertia, energies, and molecular planarity parameters.

Structure	Category	I (amu Å ²)	Energy (eV)	ΔE (eV)	MPP (Å)	SDP (Å)
	Ring	504	-85.87	0.00	0.51	2.95
	Ring	512	-85.85	0.02	0.41	2.77
	Chain	642	-85.69	0.17	0.23	1.81
	Chain	645	-85.51	0.35	0.23	1.81
	Ring	491	-85.50	0.37	0.66	2.74

To determine the sensitivity of the energetic rankings of the representative conformers to the DFT functional used, we recalculated the SA conformers with B3LYP. All other simulation details remained the same. As shown below, the ΔE values negligibly varied and the energetic rankings remain unchanged.

Table B.4. Representative conformers of SA identified through direct energy minimization with DFT, with calculated moments of inertia, and energies with both PBE and B3LYP functionals.

Structure	Category	I (amu Å ²)	PBE Energy (eV)	PBE ΔE (eV)	PBE Rank	B3LYP Energy (eV)	B3LYP ΔE (eV)	B3LYP Rank
	Ring	504	-85.87	0.00	1	-101.63	0.00	1
	Ring	512	-85.85	0.02	2	-101.59	0.04	2
	Chain	642	-85.69	0.17	3	-101.46	0.17	3
	Chain	645	-85.51	0.35	4	-101.25	0.38	4
	Ring	491	-85.50	0.37	5	-101.22	0.41	5

C. Supporting Information for Mechanistic Origins of Structure-Reactivity Effects in Polyurethane Acidolysis

Transition state generation workflow

The following section outlines the methods behind the TS generation workflow used in this paper to prepare initial guesses for the TSs of urethane and urea acidolysis. The Python codes and urethane and urea acidolysis templates used and referenced here are freely available online at https://github.com/kelsjrichardson/acidolysis_TS_generation.

1. Conformer generation (01_conf_generation.py)

To start, 50 conformers are generated for each acid using RDKit and then optimized with Universal Force Field (UFF).¹⁴³ The conformers are then cluster by Butina clustering with RDKit based on the pairwise root mean squared displacement between conformers. The unique conformers are ranked by their UFF-calculated energy, and the lowest 10 energy are selected for future calculations. These 10 conformers are saved as .xyz files and used in the next step.

2. Conformer optimization (02_convert_log_xyz.py)

We then do a geometry optimization and frequency analysis with the 10 lowest energy unique conformers in Gaussian-16 (*PBE1PBE/cc-pVTZ Opt Freq*). After this calculation, we convert the outputs from Gaussian .log files to .xyz files.

3. Align and combine acid conformers with TS templates (03_shift_key_atoms.py, 04_align_acid_template.py)

For each of the geometry optimized acid conformations, we order the atom indices such that the four atoms that participate in the six-centered TS are at a known index (e.g. 1-4 and 5-8 for DCAs). Now, the optimized acid conformers are ready to be combined with the defined

urethane and urea acidolysis templates. These TS templates contain the model urethane or urea compound as well as four placeholder atoms for the acid (acid terminal C, carbonyl O, hydroxyl O, and hydroxyl H).

First, a plane is defined with atoms 1, 2, and 4 of the TS template (acid terminal C, carbonyl O, and hydroxyl H). This plane is calculated with the same atoms of the individual acid conformer, and the acid is rotated to align the planes. Next, the vector from atoms 2 to 3 (acid terminal C and hydroxyl O) in the TS template and the acid conformer is calculated and rotated for alignment. And finally, the atoms in the acid conformer are translated until they match the acid atoms in the TS template. After checking that there is no overlap between the updated acid conformer structure and the TS template, the two structures are combined, and the acid placeholder atoms are removed. This structure, a guess for the acidolysis TS, is saved as an .xyz file and used in the next step.

4. TS refinement (urea only)

The generated structure for the urea TS is slightly farther from the actual TS than for urethane. As such, when using this workflow for urea TSs, an initial TS search/refinement is required. To do this, we used the QST3 optimization in Gaussian-16 (*PBE1PBE/cc-pVTZ Opt=(qst3, redundant) Freq*), which uses the Synchronous Transit-Guided Quasi-Newton (STQN) method to efficiently search for a TS given the reactant complex, product complex, and a TS guess (from the above workflow). The output from the QST3 calculation was then used as the input for the next step.

5. TS optimization calculation

After generating the guesses for the TS structures, we optimized these structures using Gaussian-16 (*PBE1PBE/cc-pVTZ Opt=(TS, calcFC, nofreeze, noeigentest) Freq*) to identify the

pertinent TS. We verified that each structure had one imaginary frequency and ran IRC calculations on representative TSs to confirm their validity (**Fig. S1**).

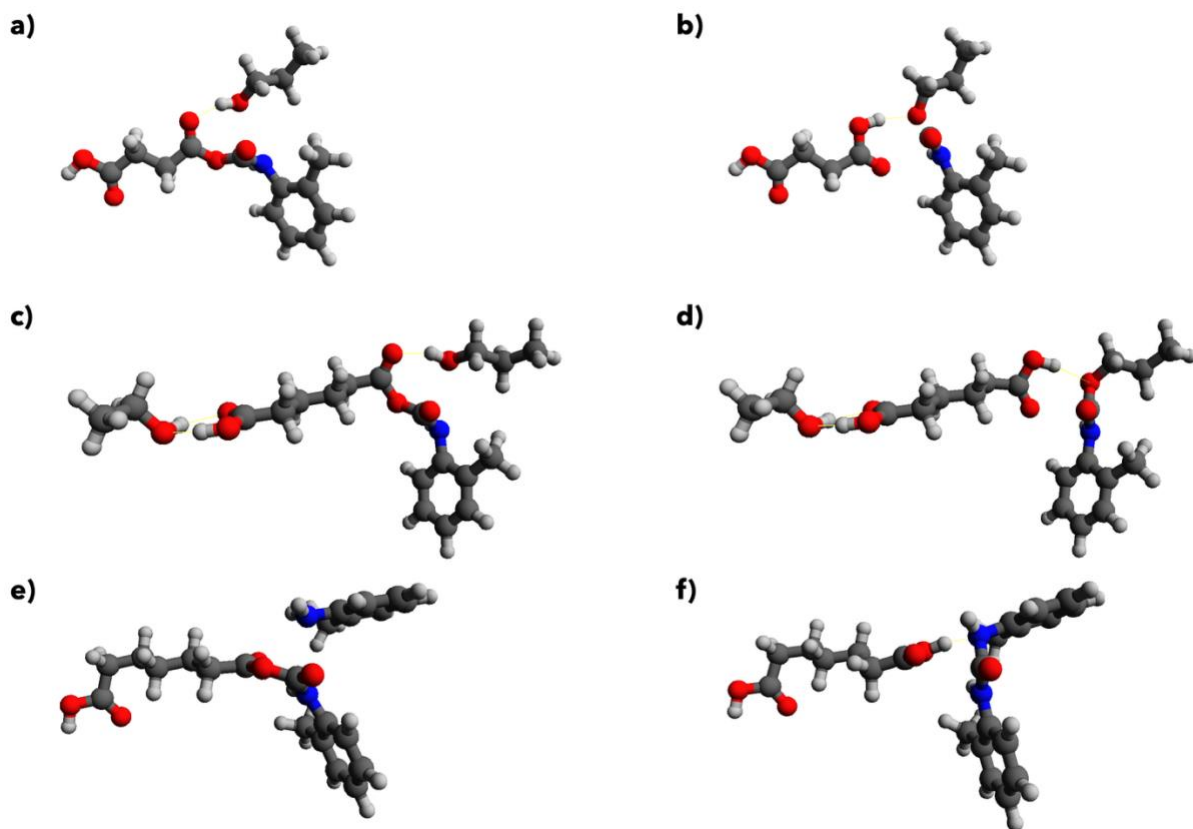


Figure C.1. IRC forward (a) and reverse (b) calculation for minimum energy SA urethane acidolysis TS. IRC forward (c) and reverse (d) calculation for minimum energy AA urethane acidolysis TS stabilized by hydrogen bonding participant (EtOH). IRC forward (e) and reverse (f) calculation for minimum energy PiA urea acidolysis TS. Computational details: Gaussian-16, PBE0, cc-pVTZ.

6. Analysis and Boltzmann weighting

For the determination of energy barriers that could be compared to experimental observables, we used the GoodVibes program to recalculate the thermodynamic values of the optimized reactants and TSs at 448.15 K (*python -m goodvibes <TS_OUTPUT_FILE> -t 448.15 -q --csv --<CSV_FILE_W_RESULTS>*).¹⁵² We used quasi-harmonic corrections to both entropy and enthalpy with a frequency cutoff of 100 wavenumbers. From these corrected

energy values, we calculated the Boltzmann-weighted enthalpy ($\Delta H^\ddagger$) and entropy ($\Delta S^\ddagger$) barriers and standard errors at 448.15 K, considering only the unique structures. The Boltzmann factor was calculated using Gibbs free energy to capture both enthalpic and entropic effects. These values are what was used for analysis in this paper.

Dicarboxylic acid chain length

Table C.1. Chain-length dependent urethane acidolysis TS calculations and results compared to experimental results. Computational details: Gaussian-16, PBE0, cc-pVTZ, T=448K. Experimental details: 175°C under inert N₂ atmosphere, 0.5 g PU, saturation acid loadings, see ref 82 for more details.

Acid	# of C b/w acid groups	# of unique TSs calc.	$\Delta H^\ddagger$ (kJ/mol)	$\Delta H^\ddagger$ Error (kJ/mol)	$\Delta S^\ddagger$ (J/molK)	$\Delta S^\ddagger$ Error (J/molK)	k_{DFT}/k_{max}	k_{exp} ($\mu\text{mol/s}$) ⁸⁹
SA	2	6	151.4	4.2	-166.0	1.9	1	2.16
GA	3	8	149.9	3.0	-182.6	4.4	0.20	1.42
AA	4	11	148.8	1.9	-182.8	1.8	0.27	0.52
PiA	5	13	150.6	2.6	-180.1	1.3	0.23	0.44

Entropic contributions: To understand the mechanistic interpretation of the DCA entropic barrier becoming more negative (less favorable) with increasing chain length, we deconvoluted the barrier into its translational, rotational, and vibrational components and compared each to the barrier for SA (**Fig. C.2**). Rotational entropy is the biggest contributor to the trend, leading to our hypothesis that a preorganization penalty for longer acids is making the reaction less favorable.

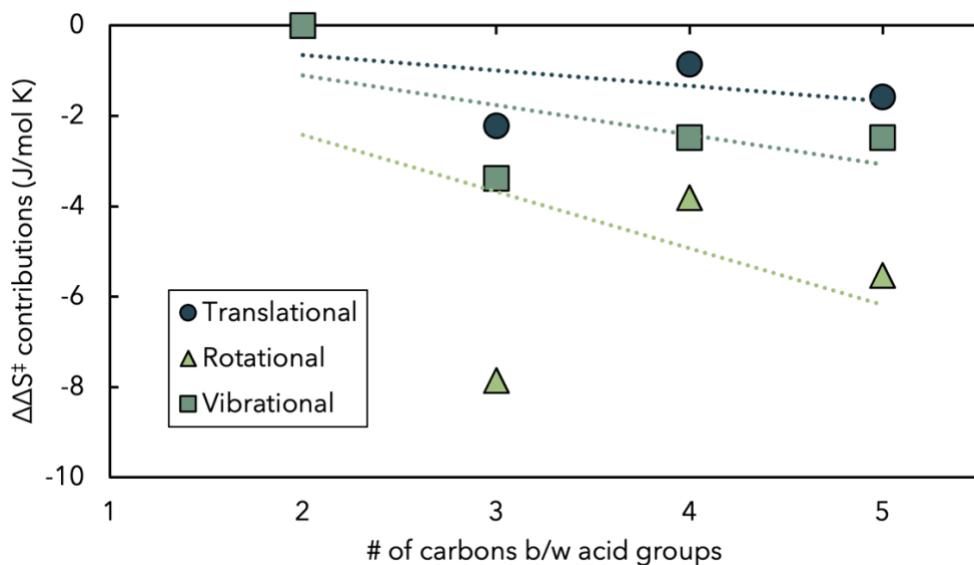


Figure C.2. Translational, rotational, and vibrational contributions to the urethane acidolysis entropic barrier with DCAs, compared to the value for SA. Computational details: Gaussian-16, PBE0, cc-pVTZ, T=448K.

H-bond participant: We wanted to determine if our results for DCAs were applicable in the presence of a hydrogen bonding participant. So, we add ethanol to our lowest-energy TS structures and recalculated the enthalpic and entropic barriers. Similar to what is seen with urea acidolysis with PiA, we observe a stabilization reducing in a reduced enthalpic barrier, but this amount is similar for all DCAs such that there is still no trend with $\Delta H^\ddagger$ and chain length (**Fig. C.3a**). Moreover, the entropic barrier still generally decreases with increasing chain length, showing that our hypotheses hold even when including intermolecular interactions (**Fig. C.3b**). Additionally, these trends still hold even if dispersion corrections (Grimme's D3 dispersion with Becke-Johnson damping) are added to the DFT calculations (**Fig. C.4**).

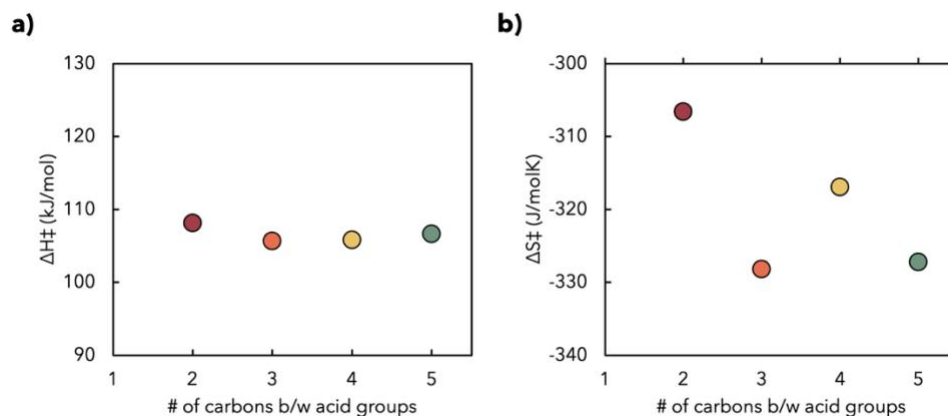


Figure C.3. Enthalpic barrier (a) and entropic barrier (b) for urethane acidolysis with DCAs stabilized by hydrogen bonding participant (EtOH). Computational details: Gaussian-16, PBE0, cc-pVTZ, T=448K.

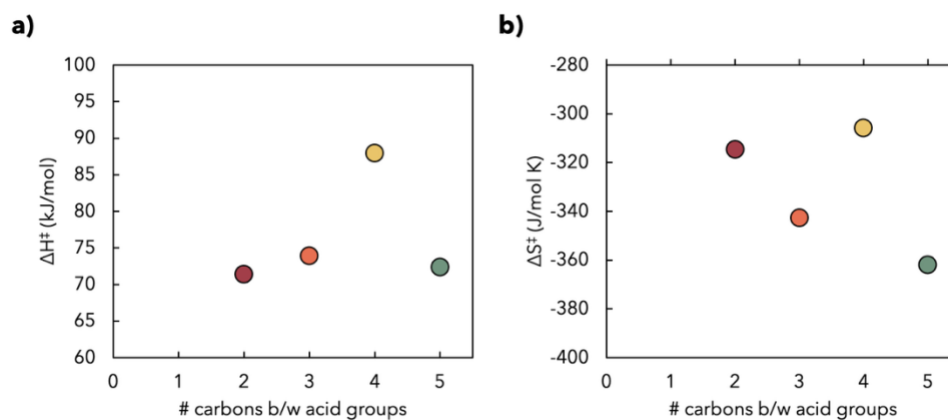


Figure C.4. Enthalpic barrier (a) and entropic barrier (b) for urethane acidolysis with DCAs stabilized by hydrogen bonding participant (EtOH). Computational details: Gaussian-16, PBE0, cc-pVTZ, T=448K, GD3BJ.

And finally, hydrogen bonding stabilized TS structures are robust to the initial position of the hydrogen bonding participant. We initialized three TS structures with ethanol in different orientations and everything else held constant (Fig. C.5, top row). After DFT optimization, all three structures optimized to the same TS (Fig. C.5, bottom row).

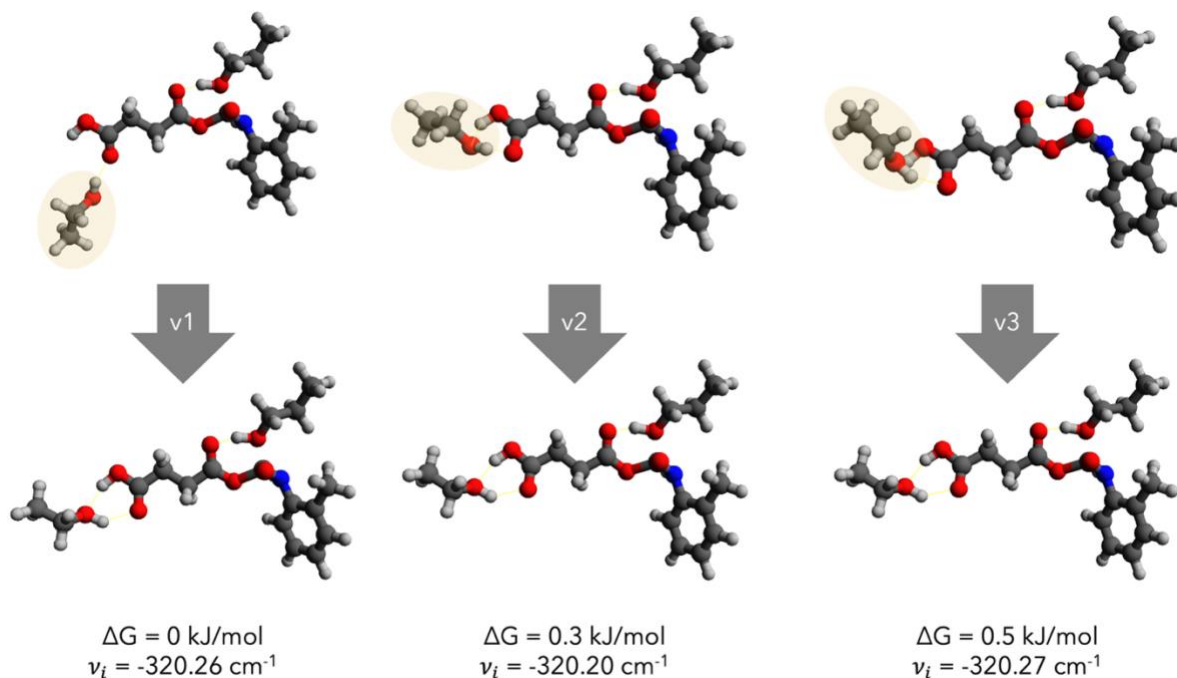


Figure C.5. SA minimum energy TS structure, initialized with ethanol in 3 different configurations, all optimize to the same minimum with the same energy and imaginary frequency. ΔG values show energetic variation with respect to v1. Computational details: Gaussian-16, PBE0, cc-pVTZ, T=448K.

Monocarboxylic acids vs dicarboxylic acids

Table C.2. PiA and HA urea acidolysis TS calculations and results. Computational details: Gaussian-16, PBE0, cc-pVTZ, T=448K.

Acid	# of acid groups	# of unique TSs calc.	$\Delta H^\ddagger$ (kJ/mol)	$\Delta H^\ddagger$ Error (kJ/mol)	$\Delta S^\ddagger$ (J/molK)	$\Delta S^\ddagger$ Error (J/molK)
PiA	2	12	116.2	1.5	-140.7	0.1
HA	1	9	115.6	2.2	-190.4	4.4

Table C.3. PiA and HA with ethanol urea acidolysis TS calculations and results. Computational details: Gaussian-16, PBE0, cc-pVTZ, T=448K.

Acid	# of acid groups	$\Delta H^\ddagger$ (kJ/mol)	$\Delta H^\ddagger$ Error (kJ/mol)	$\Delta S^\ddagger$ (J/molK)	$\Delta S^\ddagger$ Error (J/molK)
PiA	2	92.4	0	-192.1	0
HA	1	114.9	0	-264.2	0

H-bond participant: We also tested to see if other hydrogen bonding participants would result in the same observed enthalpic stabilization for DCAs. Previously, we used ethanol to approximate the functionalities in the soft polyol domains. Next, we used acetamide to act as the hard urea domains. We observed the same effect with acetamide as we did with ethanol: DCAs benefit from an enthalpic stabilization of the TS while MCAs lack the second acid group to form these stabilizing hydrogen bonds.

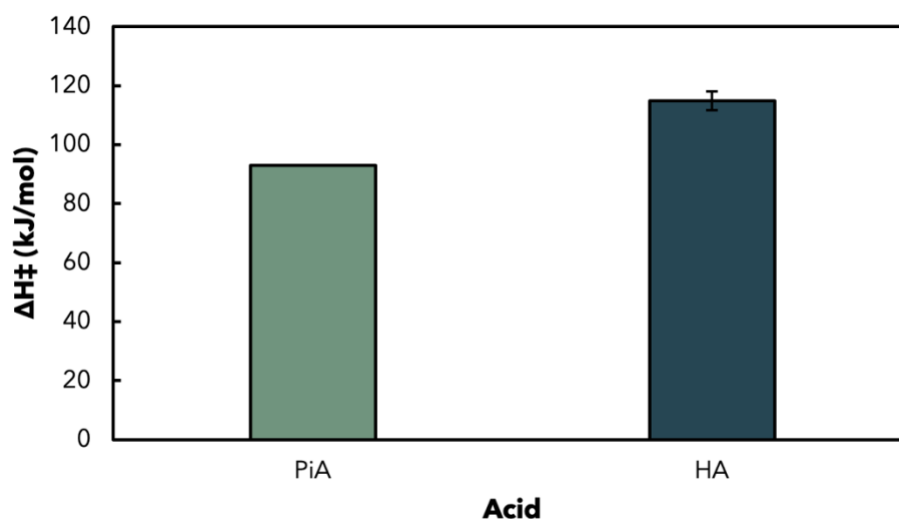


Figure C.6. Enthalpic barrier of urea acidolysis with PiA and HA stabilized by hydrogen bonding participant (acetamide). Error bars are standard deviations based on Boltzmann distribution of acid conformations and transition states. Computational details: Gaussian-16, PBE0, cc-pVTZ, T=448K.

D. Supporting Information for Glycol-dependent kinetics of uncatalyzed polyurethane glycolysis

Experimental Methods

A protocol was developed to isolate the polyol products using a series of toluene and brine washes, as illustrated in **Fig. D.1**.

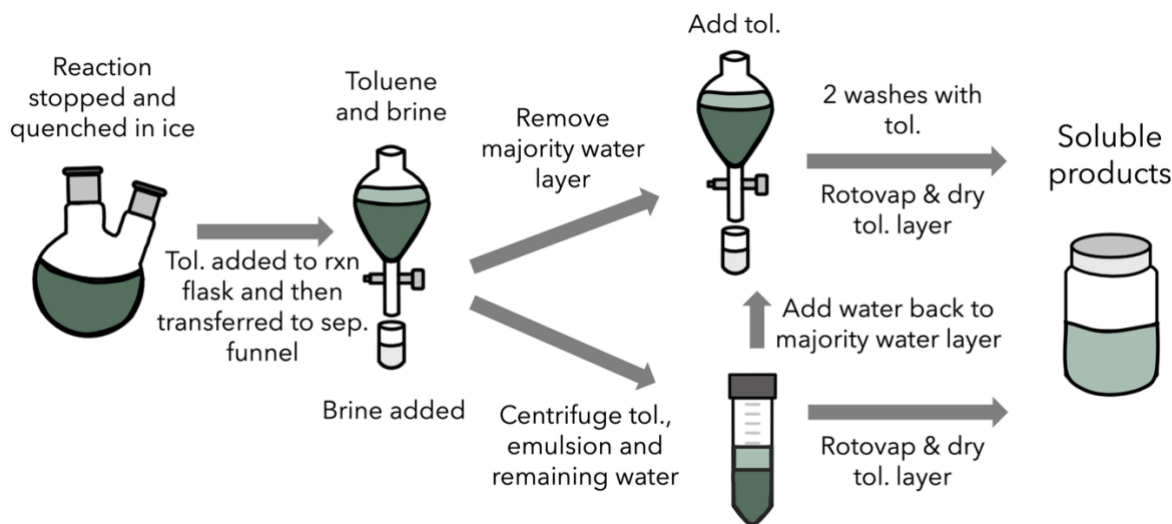


Figure D.1. Experimental isolation procedure for polyol oligomer and monomer

After isolation, the soluble products were analyzed with quantitative ^{13}C -NMR (qC-NMR). In this analysis method, the areas corresponding to propylene oxide backbone peaks (highlighted in red in **Fig. D.2**) were compared to an internal methanol standard to quantify the mass fraction of the soluble products that correspond to polyol products. To test the accuracy of this method, **Fig. D.3** shows the mass of polyol product calculated with this method compared to the actual mass of VORANOL™ 8136 Polyol used in the sample. This revealed that the qC-NMR protocol could be used to determine the soluble product purity with an estimated uncertainty of 1.5%.

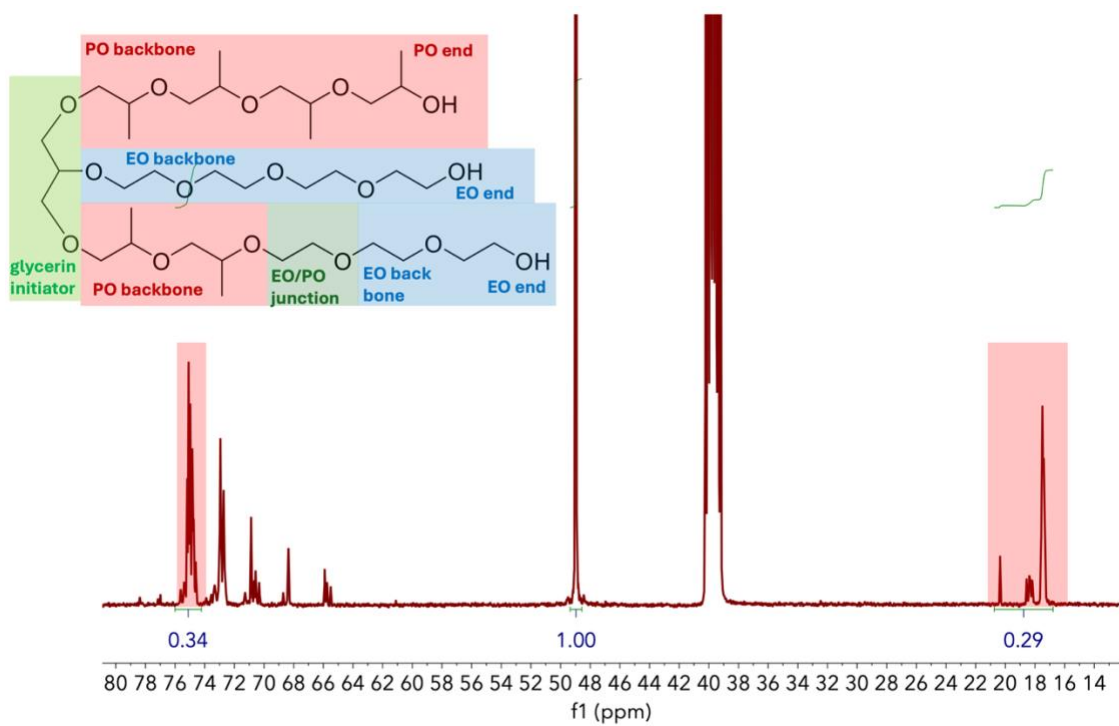


Figure D.2. Propylene oxide backbones and methyl groups used in quantitative ^{13}C -NMR

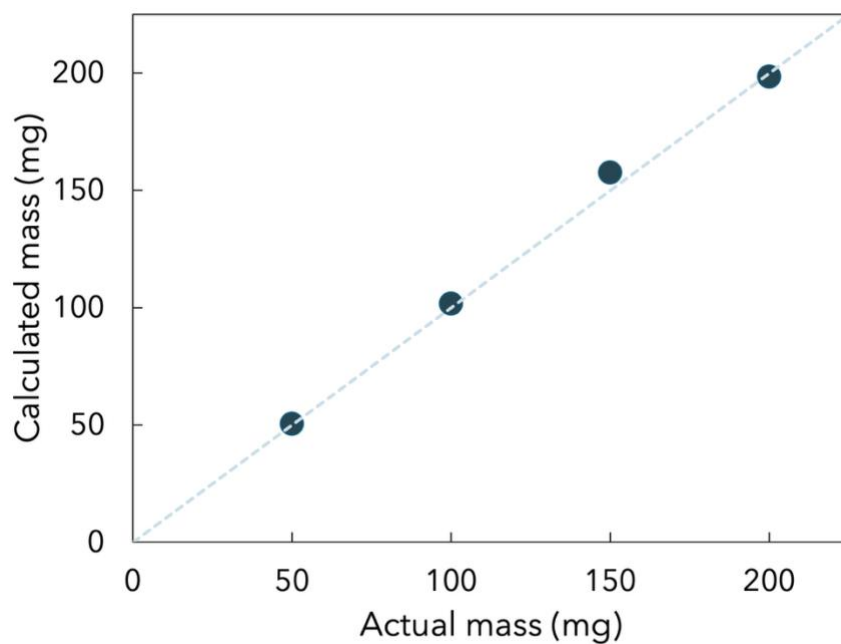


Figure D.3. Actual polyol mass vs calculated polyol mass determined by qC-NMR method

After qC-NMR, gel permeation chromatography (GPC) was used to quantify the mass fractions of monomer and oligomeric polyol. To do this, we fit the chromatograms with three Gaussian curves, corresponding to monomer, small oligomer, and large oligomer products (see Fig. D.4 for an example). We then use the area under these curves to calculate the mass fractions using the equations below:

$$f_{mon} = \frac{A_{mon}}{A_{mon} + A_{olig1} + A_{olig2}} * \frac{1}{f_{mon,V}}$$

$$f_{olig} = 1 - f_{mon}$$

This method is repeated for each time point. $f_{mon,V}$ corresponds to the monomer peak area of the GPC of VORANOL™ 8136 Polyol (Fig. D.5).

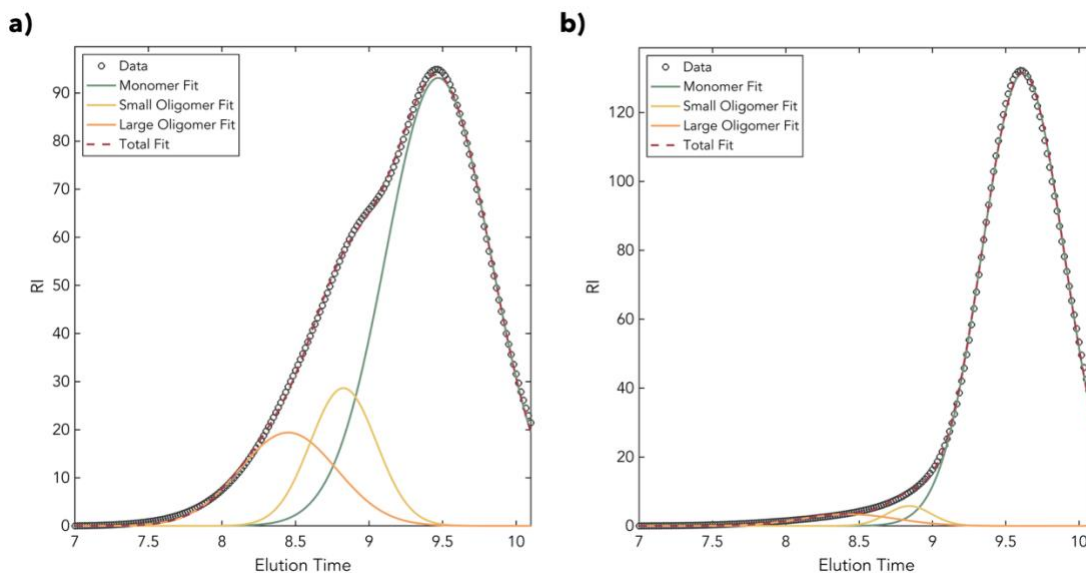


Figure D.4. Example GPC analysis showing monomer, small oligomer, and large oligomer peaks at 1 hr (a) and 24 hr (b). Experimental details: 15 mL EG, 1g PUF, 190°C.

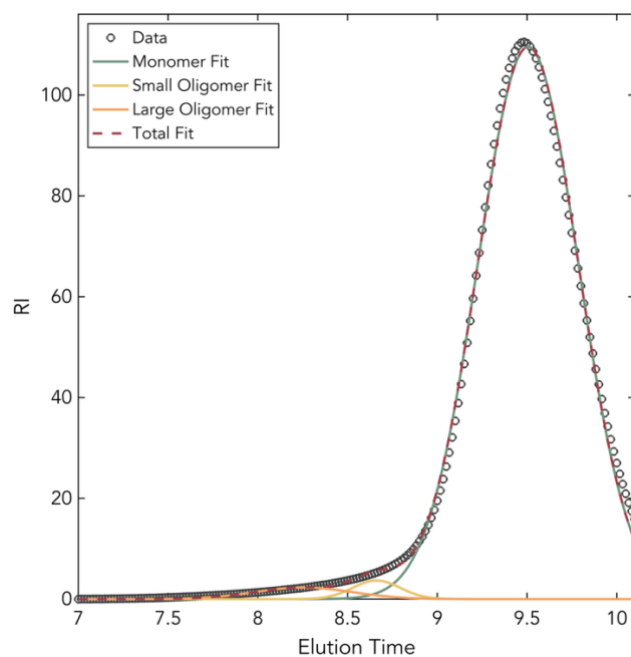


Figure D.5. GPC of monomeric VORANOL™ 8136 Polyol standard

This methodology was also repeated preliminarily with 1,5-pentanediol (15PD), as shown in Fig. D.6. Interestingly, significantly less oligomer mass is accumulated with 15PD than with EG.

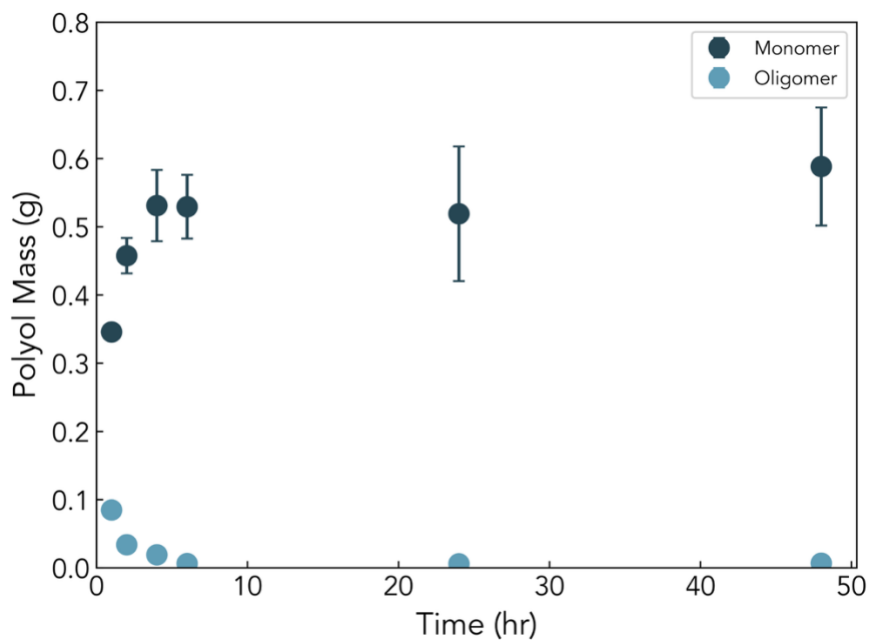


Figure D.6. Monomer and oligomer evolution with 1,5-pentanediol. Experimental details: 15 mL 15PD, 1g PUF, 190°C.

Kinetic Fitting

We also tried to fit the EG monomeric polyol evolution data using a one parameter first order fit. Notably, the one parameter fit results in significantly more error than the two-parameter sequential reaction model fitting (Fig. 6.2).

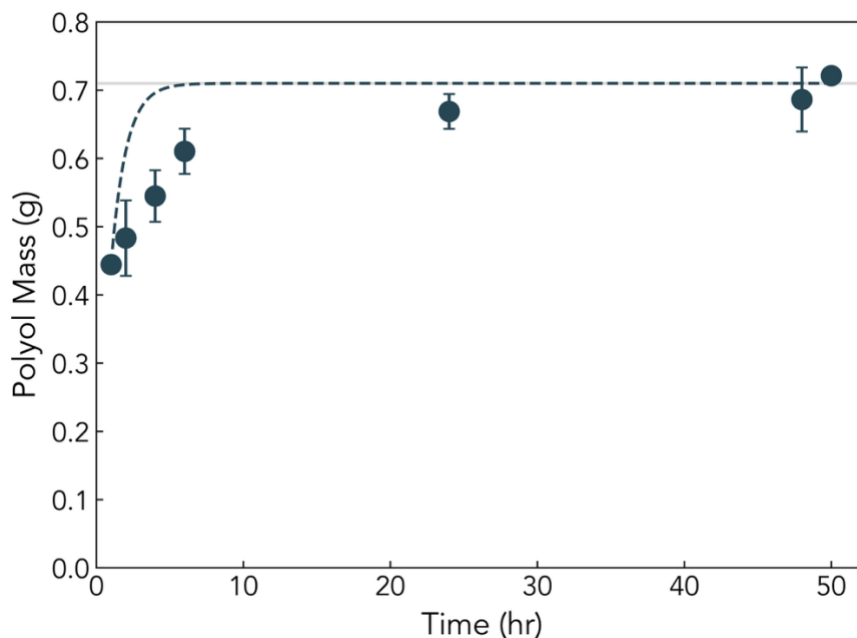


Figure D.7. One parameter first order fit for EG for model $PU \xrightarrow{k} monomer$. Experimental details: 15 mL EG, 1g PUF, 190°C.

To estimate a lower bound for k_1 , we completed a grid search of k_1 and k_2 and observed the resulting fitting error. To better see the differences in the fitting errors, we normalized the error per the protocol reported in Fig. D.8a. As shown in Fig. D.8b, when $k_1 > 1.1 \text{ hr}^{-1}$, both

the goodness of the fit and the corresponding value of k_2 do not vary. Thus, we claim that 1.1 hr^{-1} is the lower bound for k_1 .

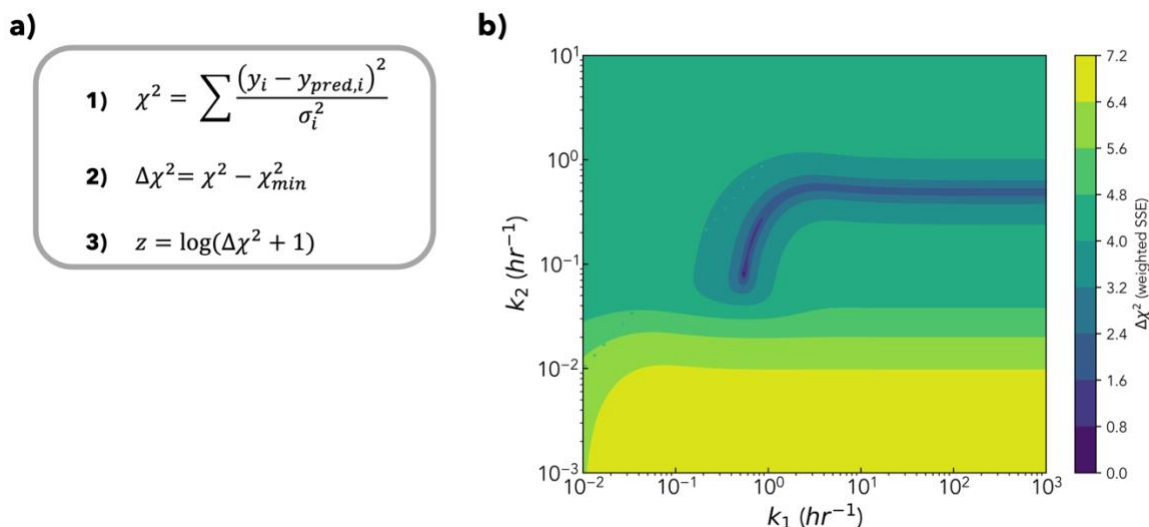


Figure D.8. Grid search of k_1 and k_2 for 15 mL EG with 1 g PUF at 190°C with weighted fitting error (calculation method described in (a)) (b).

Computational Methods

We used DFT to calculate reaction barriers for urethane and urea glycolysis at 190°C . Fig. D.9 shows the complete computational results. Fig. 6.3 does not include 2Me13PD as there is not a dielectric constant reported for this glycol.

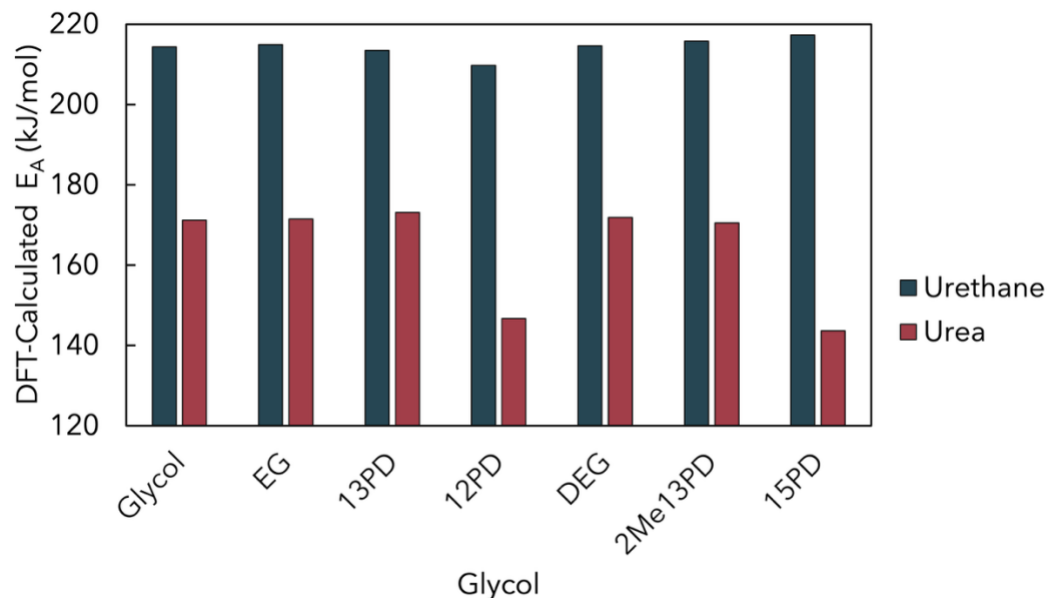


Figure D.9. DFT-calculated urethane and urea barriers for full glycol scope. Theory details: Gaussian-16, cc-pVTZ/PBE0, GD3BJ dispersion corrections, $T=190^\circ\text{C}$.

We additionally can compare the computed transition states for glycolysis to those found in acidolysis. In glycolysis, the O atom that loses the proton is also the nucleophilic atom that forms the new C–O bond to the urethane carbonyl carbon. Therefore, proton transfer and bond formation are geometrically coupled, favoring a compact four-centered transition state. In acidolysis, however, the proton-donating O–H and the bond-forming O are separated within the carboxylic acid functionality. As a result, proton transfer and bond formation are spatially decoupled, requiring a more extended cyclic arrangement that can align the proton donor, the urethane carbonyl oxygen, and the bond-forming carboxyl oxygen, which is consistent with a six-centered transition state. This comparison is shown visually in **Fig.**

D.10.

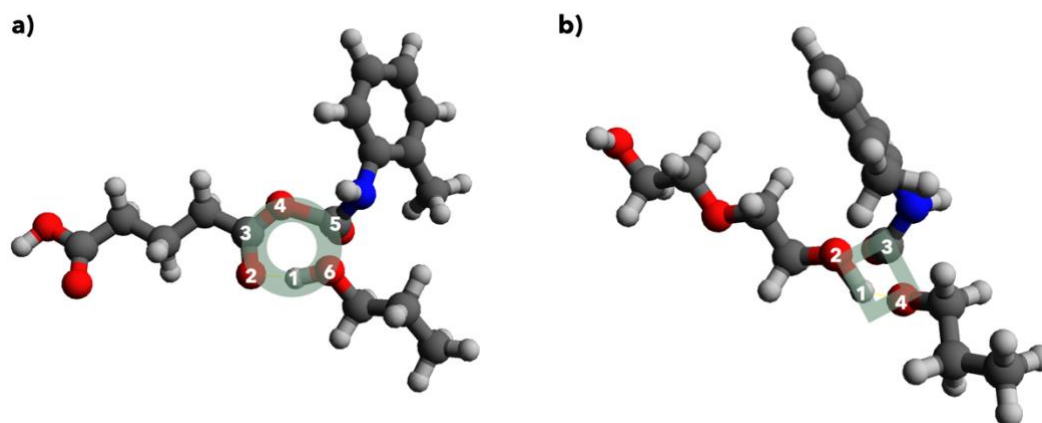


Figure D.10. a) Urethane acidolysis transition state structure with glutaric acid. Atoms in six-centered TS are marked with labels 1-6. The proton to be transferred is atom 1 and the nucleophilic O is atom 4. b) Urethane glycolysis transition state structure with ethylene glycol. Atoms in four-centered TS are marked with labels 1-4. The proton to be transferred is atom 1 and the nucleophilic O is atom 2.

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