

**Polymers Bearing Cyclic or Linear Amidines: Exploring the Physical and Chemical
Responses to the Reversible Capture and Release of Carbon Dioxide**

**A Dissertation Presented for the
Doctor of Philosophy
Degree
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DEDICATION

This dissertation is dedicated to my parents, Ted and Bobbie Chun, who covered our family in God's love and blessings. And to my sisters, Amanda and Emily Chun, who are my forever friends and support system.

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ABSTRACT

Post-combustion capture involves passing flue gases through a sorbent material to trap carbon dioxide before it enters the atmosphere. Industrial-scale carbon capture relies on aqueous amine solutions, which generate toxic byproducts, have high volatility, and require significant heat loading to release captured carbon dioxide. An alternative approach employs solid sorbents with greater stability and lower heat requirements for carbon dioxide release. Amidine-functionalized polymers have shown promise in capturing and releasing carbon dioxide reversibly at near-ambient temperatures. However, the inherent stability issues of amidines have hindered efforts to maintain high carbon dioxide capture efficiency and characterize these polymers effectively. My dissertation addresses the synthetic challenges of incorporating amidine functionality into monomers and polymers, alongside examining the physical and chemical responses during carbon dioxide capture and release. Specifically, I assessed various synthetic methods for attaching a monocyclic amidine group to acrylate- or styrene-based monomers and polymers. These studies revealed the instability of monocyclic amidines, which hydrolyze in atmospheric water, react at the vinyl site of acrylate-based monomers, and undergo alkylation reactions that compete with carbon dioxide binding. Consequently, a more stable linear amidine moiety was chosen for functionalizing styrenic polymers used to investigate reversible carbon dioxide capture and release behaviors. The resulting linear amidine-functionalized polymer exhibited significantly improved stability and solubility, facilitating ease of experimentation and thorough characterization. Notably, this polymer demonstrated exceptional carbon dioxide adsorption capacity comparable to leading porous organic polymers. Investigation into the physical and chemical dynamics of carbon dioxide binding included detailed exploration of environmental influences (e.g. moisture content, carbon dioxide concentration, inert gas and temperature swings) on capture and release

behaviors, DFT calculations to elucidate binding mechanisms at the amidine motif, comprehensive hydrolysis characterization in amidine-functionalized polymers, and assessment of thermomechanical properties as a result of hydrolysis. These studies underscore how amidines respond to diverse synthetic and environmental conditions and how these chemical modifications influence the physical properties of functionalized polymers, thereby impacting their effectiveness in carbon dioxide adsorption applications.

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CHAPTER I
INTRODUCTION

1.1 Carbon Capture and Sequestration

In recent decades, the Earth's climate has experienced notable shifts, characterized primarily by a significant rise in surface temperatures attributed largely to the emission of greenhouse gases, notably carbon dioxide (CO₂), dating back to the industrial era.¹ The combustion of fossil fuels for power generation, industrial activities, and transportation are the predominant sources responsible for the increased atmospheric concentration of CO₂. Thus, the concept of carbon capture and sequestration (CCS) was introduced to reduce CO₂ emissions. This process captures CO₂ from large scale point-sources of anthropogenic pollution, such as fossil fuel refineries and power plants, and enables concentrated amounts of CO₂ to be transported to a storage site (often by injection into suitable geological formations) in order to prevent re-entry into the atmosphere.²⁻⁵

The three most common methods of CCS are pre-combustion capture, oxyfuel combustion, and post-combustion capture. Pre-combustion of fossil fuels takes place through pyrolysis, gasification, or reforming reactions, resulting in the generation of clean gas fuels like H₂, which, upon combustion, produces water, while the carbon is transformed into a CO₂-rich effluent.⁴ In the oxyfuel combustion process, pure oxygen is obtained from cryogenic air separation or membranes. The products upon combustion are essentially CO₂ and H₂O, where CO₂ is isolated by condensing water out of the exhaust.⁶ Lastly, post-combustion capture introduces a new phase medium that traps CO₂ from the flue gas that is emitted after fossil fuel combustion. Even though the flue gas contains a CO₂ concentration of ≤ 15 vol%, the phase medium extracts highly pure CO₂ that can be used for enhanced oil recovery, urea production, or in the food/beverage industries.^{4,7} Post-combustion capture is extensively researched due to the potential to retrofit a wide range of existing power plants with this technology without major modifications. In addition to CCS, several gas separation technologies have been investigated to improve post-combustion

capture, including: a) absorption, b) adsorption, c) cryogenic distillation, and d) membrane separation.^{8–10} Among these technologies, “amine-scrubbing” by absorption is a mature technology that has proven reliable for CCS applications in power plants, iron and steel industries, cement industries and oil refineries.¹⁰ Absorption is a gas-liquid operation where the gas components are absorbed into the new liquid phase.⁴ **Figure 1.1** illustrates this reversible CO₂ capture and release process, where the flue gas is bubbled through a solution of aqueous amines to trap CO₂ at up to 0.45 mol CO₂/mol amine, which illustrates that approximately two molar equivalents of an amine, such as monoethanolamine (MEA), are required to capture one mole of CO₂.¹¹ The CO₂-rich amine is then transferred to a stripping column where it is heated to ~150 °C to desorb the captured CO₂ and regenerate the original amine. By this process, a stream of concentrated CO₂ is produced.

While demonstrating high CO₂ capture efficiency and good chemical reversibility, this technology suffers from several drawbacks, including the high heat load necessary for amine regeneration, the generation of toxic byproducts from thermal and oxidative degradation of amines, and the loss of amines through volatilization. These make amine scrubbing an energy-intensive process with significant environmental implications. In an effort to make more durable sorbents and to reduce the heat loading required for regeneration, extensive research in CO₂ adsorption by solid sorbents has been explored.

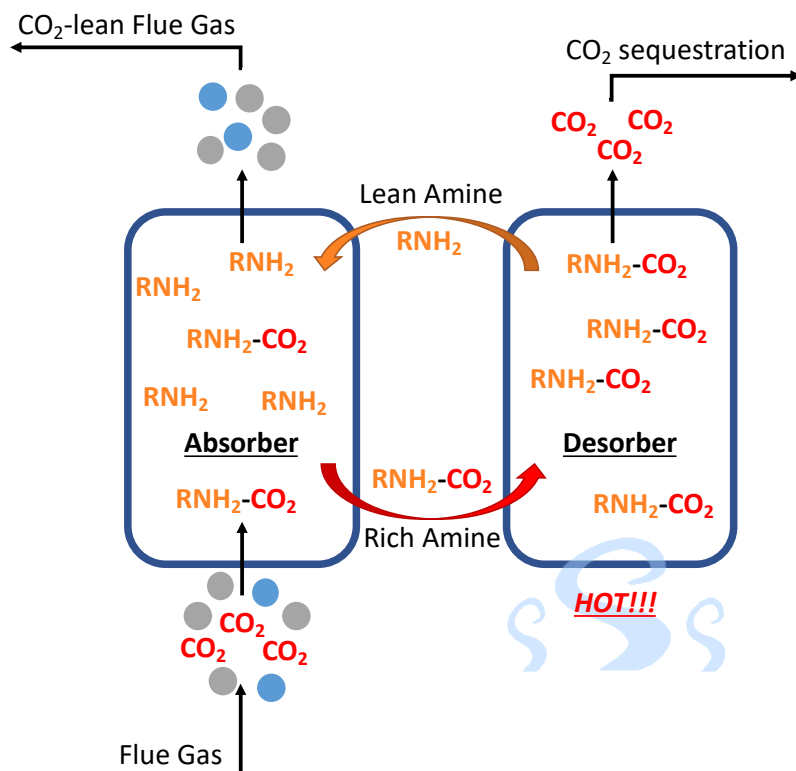


Figure 1.1. Illustration of a modern-day “amine-scrubbing” system. Flue gas is bubbled through a solution of aqueous amines that selectively traps CO_2 . The CO_2 -rich amine is transferred to a desorption column where the CO_2 is released at high temperature and the sequestered for further use. The lean amine is then recycled to repeat the adsorption/release process.

1.2 CO₂ Adsorption by Solid Sorbents

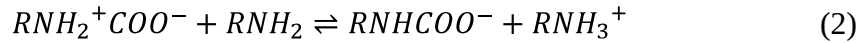
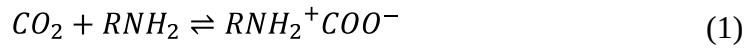
The shortcomings of amine-based absorption for CO₂ sequestration, such as the high heat loading requirements, low gas-liquid contact areas, and the lack of chemical and physical durability (e.g. the degradation and volatility of aqueous amines) have shifted the attention towards adsorption processes. Adsorption involves a fluid-solid interface in which molecules from the gas stream are attracted to the surface of the solid sorbent, most commonly by physical forces (physisorption). In the context of CO₂ adsorption, physisorption is desired due to the ability to capture and release CO₂ in a reversible manner (repeated over several cycles without loss of capture efficiency) at relatively low heat loading and atmospheric pressure. Although the weak interactions of physisorption aid in reversibility (capture and release), it also results in a much lower CO₂ capture efficiency compared to a chemisorption process. Therefore, the tradeoff exists where adsorption provides good reversibility (low heat loading) but low CO₂ capture efficiency, while absorption provides poor reversibility (high heat loading) but high CO₂ capture efficiency. To address the issues related to weak adsorption, several researchers have sought to increase the surface area of solid sorbents through strategies such as porous organic polymers (POPs) and metal-organic frameworks (MOFs), while preserving reversible capture and release characteristics.^{12–17} This approach has yielded notable enhancements in CO₂ capture efficiency. Another effective approach entails using functional groups with enhanced CO₂ capture efficiency, leading to materials that surpass the CO₂ capture performance of contemporary amines like MEA, which is commonly used in scrubbing systems. These functional groups can be affixed to polymers, thereby offering advantages such as facile tunability, improved solubility, and simplified characterization compared to MOFs or POPs. The use of modified polymers offers a

way to study different CO₂-adsorbing groups influence the system's physical and chemical properties.

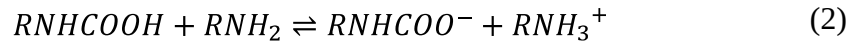
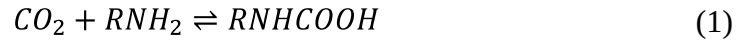
1.3 Mechanism of CO₂ Capture by Aqueous Amines

Understanding the CO₂ capture efficiency of aqueous amines, like MEA, hinges on comprehending the mechanisms through which these substances capture CO₂. MEA is specifically highlighted here due to its widespread use in amine scrubbing systems. The mechanism has been debated for some time, and the two most significant proposals are the 1) capture of CO₂ through a zwitterionic intermediate,¹⁸⁻²² which is shown by Eqns 1 and 2, or 2) capture through a carbamic acid intermediate,²³ which is shown by Eqns 3 and 4.

Zwitterion Intermediate:



Carbamic Acid Intermediate:



While most of the existing works agree on the zwitterion mechanism, a recent report by Lv et al. presents a clearer picture of the CO₂ adsorption mechanism through the use of ¹³C NMR studies. They noted that the reaction pathway between MEA (30 wt% in aqueous solution) and CO₂, which is shown in **Figure 1.2**, changed as the CO₂ loading increased.²⁴ At low CO₂ loading, a fast reaction between CO₂ and MEA yields a zwitterion intermediate. At this point, another MEA instantaneously neutralizes the zwitterion by deprotonation and stabilizes the resulting carbamate

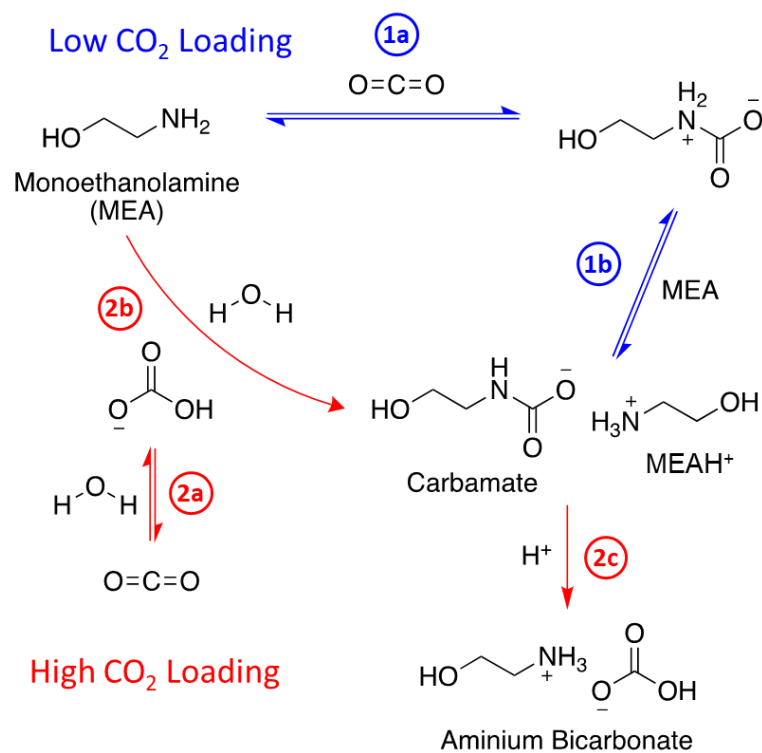
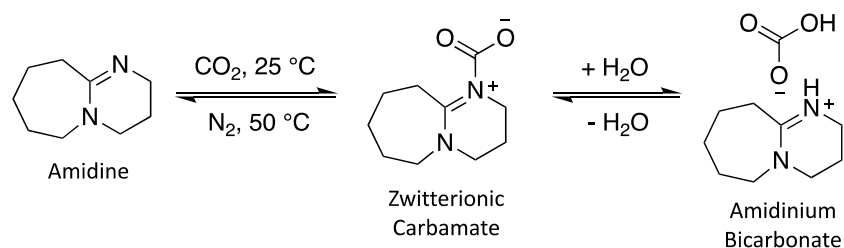


Figure 1.2. Mechanism for CO₂ absorption by monoethanolamine (MEA) proposed by Lv and coworkers. The pathway resulting from low CO₂ loading is depicted by the blue arrows, while the pathway resulting from high CO₂ loading is depicted by the red arrows.

through electrostatic interactions. This pathway, shown by the blue reaction arrows, results in CO₂ capture efficiency of 0.40 mol CO₂/mol MEA, meaning that the system is nearly saturated (maximum capture efficiency is 0.45 mol CO₂/ mol MEA) even at low CO₂ loading.¹¹ Upon increasing the CO₂ loading, the pH of the solution decreases. At this point, hydration of the CO₂ was enhanced, as shown by step 2a, which increases the formation of HCO₃⁻ that subsequently reacts with MEA to temporarily form the carbamate. Due to the low pH, the carbamate is unstable and readily reacts with H⁺ to form the bicarbonate. The unstable formation of the carbamate may explain why previous works^{23,25,26} proposed carbamic acid as the intermediate (Eqns 3 and 4), where the carbamate could be mistaken for the carbamic acid due to the quick transformation.

1.4 Mechanism of CO₂ Capture by Amidines

In contrast to amines, which require two molar equivalents to capture one mole of CO₂, amidines can capture CO₂ at an equimolar ratio. In addition, amidines can capture and release CO₂ at near ambient temperatures, which is more energy efficient compare to the high heat loading required to desorb CO₂ in amine-scrubbing systems. This reversible process is illustrated in Scheme 1.1, which shows the generally accepted mechanism for the capture of CO₂ that applies to amidines. In this example, the amidine 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) first captures CO₂ at ambient temperature, forming the zwitterionic carbamate. In the presence of water, CO₂ reacts to form carbonic H₂CO₃, which can protonate DBU. The resulting HCO₃⁻ is then bound to the protonated DBU by electrostatic interactions to yield the amidine bicarbonate. This interaction is completely reversible by bubbling an inert gas such as nitrogen or argon through the aqueous solution at a slightly elevated temperature (50 °C). Although this is the generally accepted mechanism, the formation of the zwitterion under anhydrous conditions has



Scheme 1.1. The generally accepted mechanism for CO_2 capture by amidine compounds is shown, with DBU is used as an example. In anhydrous conditions, the amidine captures CO_2 to form a zwitterionic carbamate. A reaction between CO_2 and water results in the formation of H_2CO_3 that then protonates the amidine. When this occurs, the CO_2 is captured as a bicarbonate anion that is associated with the resulting protonated amidine.

acid, been debated for some time due to the inability to isolate and characterize it. For instance, Jessop and coworkers demonstrated that the bicyclic amidine, DBU, does not form an isolatable zwitterionic adduct with CO₂ under anhydrous conditions; rather, the bicarbonate salt, [DBUH⁺][HCO₃⁻], is formed in the presence of water, and this can be isolated and characterized.²⁷ Similarly, other organic bases have been reported to form stable adducts with CO₂ in the bicarbonate form, such as N-heterocyclic carbenes,^{28,29} N-heterocyclic olefins,^{30,31} phosphorous ylides,^{32,33} and amidine heterocycles.³⁴⁻⁴¹ However, Villiers and coworkers isolated and characterized the first nitrogen-base-CO₂ zwitterionic adduct by exposing a bicyclic guanidine, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), to CO₂ under anhydrous conditions, which yielded the TBD-CO₂ zwitterion as shown in **Figure 1.3**. This provided the first unequivocal experimental proof that the zwitterion is formed and can be isolated.⁴² However, the zwitterionic adduct for the bicyclic amidine, DBU-CO₂, could not be isolated. The stability of TBD-CO₂, which was maintained up to 40°C, was ascribed to the elevated basicity of TBD and the intermolecular and intramolecular hydrogen bonding interactions between the N-H group of TBD and the oxygen from the carboxylate group, as shown by the structure in **Figure 1.3**.

1.5 Amidines for High CO₂ Fixing Efficiency

Among the earliest and most significant demonstrations of amidine binding interactions with CO₂ is the report by Jessop and coworkers on reversible nonpolar-to-polar solvent switchability.⁴³ They found that a 1:1 mixture of the two non-ionic liquids DBU and 1-hexanol is converted into an ionic liquid upon bubbling CO₂ through the liquid mixture at atmospheric pressure and room temperature. The ionic liquid mixture is readily converted back to a non-ionic liquid mixture by bubbling N₂ or argon through the system at room temperature or, for a more

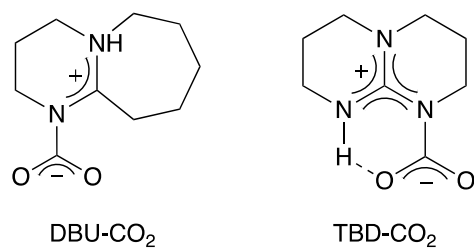


Figure. 1.3. Zwitterionic carbamate adducts as a result of CO₂ capture by DBU and TBD, where the TBD-CO₂ adduct is more stable due to the hydrogen bonding interactions between the N-H group and the oxygen in the carbamate.

rapid reaction, at 50 °C. When these two ionic liquids are dissolved in decane, the solvent switchability is observed by the appearance of a biphasic solution after bubbling CO₂ through the mixture as shown in **Figure 1.4**. These switchable mixtures of various amidine and alcohols came to be known as binding organic liquids (BOLs) and extensive research has broadened the scope of their applications.^{44–48} Soon after, Liu and Jessop discovered that an amidine with a long alkyl chain, N'-hexadecyl-N,N-dimethylacetamidine, acts as an emulsifier in its protonated state and a demulsifier in its deprotonated state. Protonation was triggered by shaking N'-hexadecyl-N,N-dimethylacetamidine in a crude oil/water mixture under a CO₂ atmosphere, creating a uniform emulsion that was stable for up to 15.5 hours. Deprotonation was then triggered by the shaking under an argon atmosphere, and two separate layers were visible after only 30 mins.⁴⁹ These studies laid the groundwork for comprehending the reversible protonation and deprotonation of amidines upon exposure to CO₂ and argon.

These works inspired explorations of a range of amidine compounds to optimize CO₂ capture efficiency for potential applications in CCS systems. Endo and coworkers pioneered these studies by analyzing amidine derivatives that varied in the degree of substitution and steric hindrance at the amidine, and how those properties affected CO₂ adsorption capacity. For instance, Aoyagi et al. determined that increasing the nucleophilicity and decreasing the steric hindrance of the amidine increases the CO₂ adsorption capacity.³⁴ As an example, the linear amidine N,N-dimethyl-N'-octylacetamidine (DMOA), the bicyclic amidine 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU), and the monocyclic amidine 1-methyl-1,4,5,6-tetrahydropyrimidine (MTHP) were separately dissolved in anhydrous acetonitrile, and exposed to dry CO₂ by bubbling a stream through the solutions. The appearance of solid precipitates for

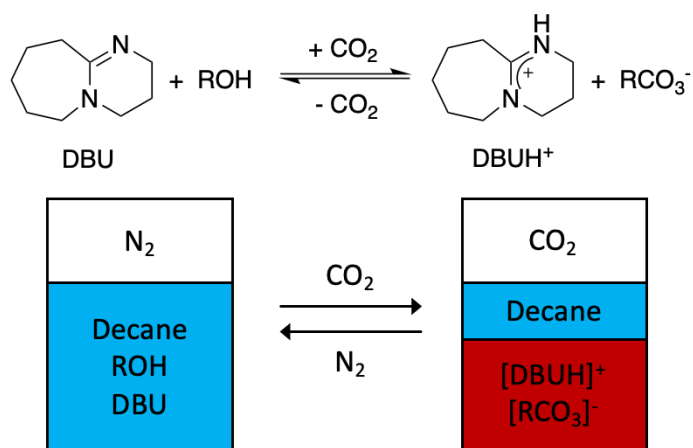


Figure 1.4. A mixture of an alkanol (ROH) and DBU acts as a switchable solvent, as demonstrated by the behavior of the mixture when combined with decane solvent. The decane, ROH, and DBU are miscible when bubbled with N₂ gas. Exposure to CO₂ bubbling results in protonation of the DBU and the reaction of CO₂ with the alkanol to form the bicarbonate. The charged bicarbonate and amidinium species yield a polar solution that is immiscible with decane, resulting in the biphasic solution shown on the right.

DBU (39% yield) and MTHP (95%) yield indicated successful conversion to the bicarbonate salt, however, DMOA did not yield any precipitate. Therefore, a much stronger CO₂ binding was demonstrated for DBU and MTHP, which can be attributed to the increased nucleophilicity owing to their cyclic structures. However, MTHP exhibits the highest yield since the monocyclic structure behaves as a much stronger nucleophile in comparison to the more sterically hindered bicyclic DBU. In addition, each amidine was subjected to CO₂ bubbling experiments in wet acetonitrile to study the effect of moisture on the CO₂ adsorption capacity. The monocyclic amidines, MTHP and 1,4,5,6-tetrahydropyrimidine (THP), exhibited negligible differences in CO₂ adsorption capacity under both dry and wet acetonitrile. The bicyclic and linear compounds, however, experienced a dramatic increase in CO₂ adsorption for the wet conditions. For instance, DBU increased its CO₂ adsorption capacity from 39% (dry) to 91% (wet). Although greater capacities were observed in wet (humid) conditions, dry conditions are optimal for fundamental research on the CO₂ capture of amidines due to the susceptibility of amidines to hydrolyze in environments with heat and moisture. The presence of moisture is potentially problematic during the CO₂ release cycles that require elevated temperatures to facilitate desorption. Therefore, the data reported by Aoyagi et al. suggest that MTHP and THP are ideal candidates for CO₂ capture because they maintain a high CO₂ adsorption capacity in dry conditions while allowing for experimental control of hydrolysis. Researchers have taken advantage of the highly efficient THP and MTHP molecules by incorporating them into polymers for solid CO₂ sorbents. These investigations on small molecule amidines provide critical insight to the parameters affecting CO₂ adsorption. For example, these works showed the importance of factors such as moisture, nucleophilicity of the amidine, and steric hindrance, showing that increased nucleophilicity and lower steric demand can enhance the CO₂ adsorption of amidines in solution. These works provide a foundation for identifying basic

physicochemical behaviors of amidines, which may be useful for efforts to implement these organic materials as solid sorbents in CO₂ capture systems.

1.6 Amidine-Functionalized Solid Sorbents

The first known report of amidine-functionalized polymers as CO₂ solid sorbents was reported by Endo et al.⁵⁰ An amidine-functionalized monomer was first synthesized by functionalization of 4-vinylbenzyl chloride with diaminopropane followed by a ring-closing mechanism and subsequent deprotonation to yield a styrene-based monomer containing the monocyclic amidine pendant, 1,4,5,6-tetrahydropyrimidine (THP). Through subsequent aqueous free radical polymerization followed by deprotonation, the reaction yielded a THP-functionalized polymer containing a styrenic backbone, which is referred to here as poly(THPSt). In solution-based CO₂ bubbling experiments, this polymer demonstrated high fixing efficiency and reversible capture/release at ambient temperature. For instance, a dimethylformamide (DMF) solution containing the small molecule bicyclic amidine, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), required 100 h to reach a CO₂ fixing efficiency of 89%, but poly(THPSt) only required 1 h to achieve a 73% fixing efficiency when dissolved in dry DMF. Unfortunately, as a solid, poly(THPSt) only achieved 12% fixing efficiency and required a long adsorption time (> 8 h). Although solid sorbents are safer for the environment, since there is no loss of sorbent due to volatilization, and amenable to a wide array of processing methods, Endo et al. observed a detrimental loss in CO₂ fixing efficiency of the solid sorbent compared to the sorbent dissolved in DMF. In addition, because the protonated form of the monomer requires aqueous polymerizations, the approach limits the ability to tune the system through the selection of comonomers and functional groups that are compatible with aqueous polymerizations.

Other works have attempted to improve on Endo's work by exploring linear polymers with amine, imidazole, or amidine functionalities, as displayed in **Table A1**.^{51–56} For instance, Furusho et al. performed CO₂ adsorption experiments on polyamidine, containing amidine functionality within the polymer backbone. In the solid state, polyamidine resulted in only a 3.4 mol% CO₂ capture efficiency (mmol CO₂/mmol amidine) after 500 h. However, mechanically blending the polyamidine with a low molecular weight poly(ethylene glycol), PEG₄₀₀, which is known to be CO₂-philic, yielded a colorless oil that achieved 66 mol% CO₂ capture efficiency in 200 h. Although this CO₂ capture efficiency is competitive with poly(THPSt) reported by Endo et al., the extended time required for CO₂ capture by the polyamidine/PEG₄₀₀ blend greatly exceeds that of Endo's poly(THPSt) solid sorbent. In addition, the polyamidine/PEG₄₀₀ blend is an oil at room temperature. This makes processability of the system more difficult, reduces overall permeability, and lowers surface area to gas contact compared to solid sorbent powders. Although Endo's poly(THPSt) is a highly efficient polymer for CO₂ capture, the cumbersome process required to synthesize THP-functionalized polymers motivated Ochiai and coworkers to explore DBN-functionalized polymers because they displayed good levels of CO₂-fixing and were easier to access synthetically.⁵⁶ A copolymer of styrene and 4-vinylbenzyl chloride (51:49 molar composition) was functionalized with DBN at the chlorinated repeat units to obtain the DBN functionalized polymer, P2DBN. Exposure of P2DBN to a flow of pure CO₂ at 25 °C resulted in a 28 mol% CO₂ fixing efficiency. A DBN-functionalized homopolymer, P1DBN, was also synthesized, however, the homopolymer resulting in a lower CO₂ adsorption capacity than P2DBN, likely due to the electrostatic interactions the amidinium bicarbonate motifs that results in polar ionic interactions that form an insoluble polymer network leading to lowering the ability of CO₂ to penetrate the system. These network formations resulted in the insolubility of all DBN-

functionalized polymers in common organic solvents after isolation. Although P2DBN achieves a higher CO₂ capacity compared to poly(THPSt) when compared in the solid state, P2DBN demonstrates even lower solubility in common organic solvents, resulting in polymers that are limited in characterization techniques and processibility.

In an effort to exploit the ring-opening reactivity of poly(2-vinyl-4,4 dimethylazlactone) (PVDMA), Barkakaty et al. used the THP-based alcohol, 4-(N-methyltetrahydropyrimidine)benzyl alcohol (PBA), to add amidine-functionality to the polymer yielding the PVDMA/PBA conjugate.⁵⁷ The benefit of post-polymerization modification of PVDMA is the polymer's hydrolytic stability and its facile reaction with nucleophiles such as thiols, alcohols, and primary amines without the formation of side products. When exposed to a stream of pure CO₂ at 25 °C, the PVDMA/PBA conjugate exhibited a CO₂ fixing efficiency of ~10-11% in 50 min,⁵⁷ which is comparable to the fixing efficiency of the poly(THPSt) solid sorbent studied by Endo et al.⁵⁰ Unfortunately, intra- and intermolecular hydrogen bonding between the THP moiety and the amide linkage, resulting from ring opening of the azlactone ring, resulted in insolubility in organic solvents and limited the ability to characterize the PVDMA/PBA conjugate. For instance, Barkakaty and coworkers noted that the polymer could not be dissolved in any solvent for NMR analysis. As a result, FTIR spectroscopy was used to assess the ratio of unreacted and reacted VDMA rings. In addition, they noted that intra- and intermolecular hydrogen bonding could be hindering CO₂ adsorption by creating an electrostatic network that competes with CO₂ fixation at the amidine, as demonstrated previously by Ochiai et al.⁵⁶

As demonstrated by these works involving amidine-functionalized polymers, insolubility due to physical crosslinking is a common issue. Therefore, Sakuragi et al. examined the crosslinking behavior of poly(THPSt) with a random copolymer of acrylic acid and n-butyl acrylate.⁵⁸ When

poly(THPSt) was dissolved in methanol and then bubbled with CO₂, the resulting polymer yields protonated amidine groups due to the trapping of CO₂ in the form of a bicarbonate. These charged repeat units form amidinium-carboxylate salt bridges between the protonated THP motif and the acrylic acid of the random copolymer to yield a supramolecular polymer gel as shown in **Figure 1.5**. FTIR measurements were used to prove the formation of the amidinium-carboxylate salt bridge by the disappearance of the C=O stretch from HCO₃⁻ at 1627 cm⁻¹, disappearance of the acrylic acid peak at 1704 cm⁻¹, and the appearance of the amidinium cation at 1682 cm⁻¹. Similar work by Furusho et al. provided evidence of crosslinking between the amidine repeat units of polyamidine and the carboxylate end groups of polybutadiene. They used diffusion-ordered NMR spectroscopy (DOSY) to confirm that a supramolecular polymer gel was formed, as indicated by the drastic reduction in the diffusion coefficient of the supramolecular polymer gel compared to the original parent polymers.

Despite the small molecule studies by Endo et al. that claimed low CO₂ adsorption for linear-type amidines in solution,³⁴ polymers functionalized with linear amidines (as opposed to cyclic amidines such as THP) have been incorporated into polymers for CO₂-sensing applications and possessing better solubility, which enables solution-state characterizations and film casting from solution. For instance, Guo and coworkers used Cu-catalyzed azide-alkyne cycloaddition (CuAAC) “click” chemistry to functionalize poly(4-vinylbenzyl chloride) with linear amidine side groups.⁵⁹ The resulting CO₂-reponsive polymer exhibited a reversible hydrophobic-to-hydrophilic transition when alternately bubbling to CO₂ and N₂, respectively, through a CHCl₃/water biphasic solution. Similarly, Swager et al. synthesized an styrene-based monomer containing an oligo(ethylene glycol) chain end-capped with a terminal azide, copolymerized this

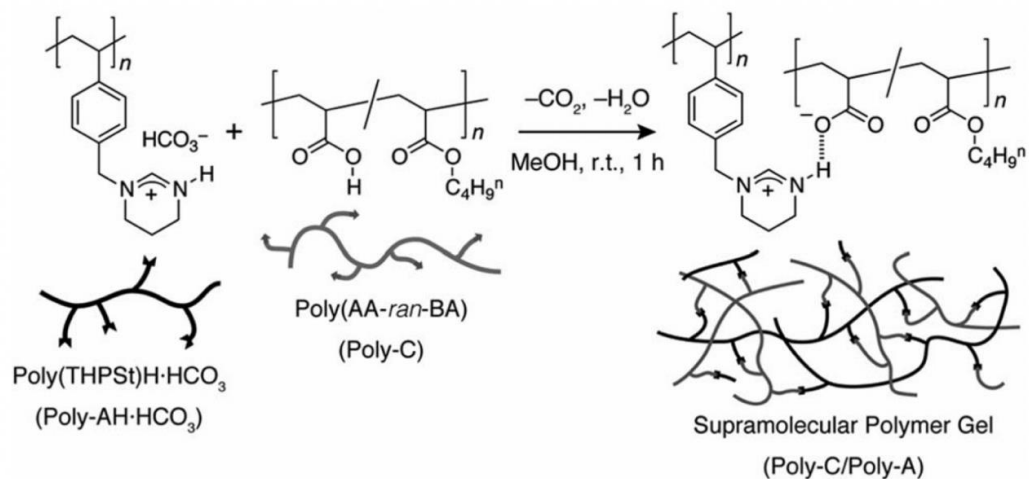


Figure 1.5. Schematic illustration for the synthesis of supramolecular polymer gels by the formation of amidinium-carboxylate salt bridges between the protonated amidine motifs in poly-AH·HCO₃ and the carboxylate groups in poly-C.

monomer with 4-vinylpyridine, and then modified the copolymer using CuAAC to install linear amidines in a manner analogous to Guo et al.⁵⁹ This copolymer was wrapped around single-walled carbon nanotubes and the resulting hybrid material used for CO₂ sensing. Experiments utilizing a mixed gas stream of CO₂ and N₂ showed that these polymer wrapped carbon nanotubes had a CO₂ detection limit of 0.2%.⁶⁰

1.7 Overview of Dissertation

This dissertation focuses on how CO₂ adsorption capacity is affected by changes in the physical and chemical properties of amidine-functionalized copolymers. Chapter II describes my preliminary efforts to synthesize THP-functionalized copolymers derived from polyacrylate, which has a less rigid backbone (for example, compared to a styrenic polymer). This effort aimed to address the solubility challenges encountered with polyTHPSt, as documented by Endo et al.⁵⁰ The first goal was to THP-functionalize the acrylate monomer, 2-hydroxyethyl acrylate (2-HEA), and this was approached by two synthetic routes: 1) the Mitsunobu reaction and 2) tosylation of 2-HEA followed by THP-substitution. Unfortunately, neither approach was successful, as described in Chp 2. To avoid the problems associated with acrylate-based amidine-containing monomers, we chose to pursue THP-functionalization of the styrene-based monomer, 4-vinylbenzyl chloride (VBC), similar to the approaches used by Endo et al.⁵⁰ to yield the desired THP-functionalized styrene, THPSt. Unfortunately, THPSt could not be polymerized by free-radical polymerization techniques in organic solvent. Therefore, post-polymerization modification of poly(St-*ran*-VBC) using Finkelstein reaction conditions was pursued to afford the THP-functionalized copolymer, poly(St-*ran*-THPSt). However, the prevalence of THPhydrolysis due to ambient moisture resulted in partial loss of the amidine functionality as a result of ring-opening.

Due to these issues, it was decided to direct efforts toward the synthesis of copolymers containing linear amidines, similar to those synthesized by Guo et al.[ref] and Swager et al.[ref]

Chapter III describes the synthesis of a series of linear amidine-functionalized copolymers and explores their physical and chemical properties as well as CO₂ adsorption behaviors. The CO₂ adsorption of the linear amidine-functionalized copolymers were studied using thermogravimetric analysis at high concentrations of CO₂ and direct air capture at low concentrations of CO₂. The molecular basis of CO₂ binding was studied using neutron vibrational spectroscopy (NVS) combined with density functional theory (DFT) calculations to gain insight on the binding of CO₂ with the amidine moiety. In addition, we used ¹H NMR spectroscopy and ATR-FTIR spectroscopy to characterize the chemical changes of poly(St-*ran*-VBTA) due to hydrolysis of the amidine. Hydrolysis also induces changes in thermomechanical properties, such as glass transition temperature (T_g) and degradation temperature (T_d), which were analyzed by dynamic scanning calorimetry (DSC) and TGA. Finally, Chapter IV summarizes the work presented in this dissertation and offers perspectives on additional routes of investigation stemming from this effort.

APPENDIX A

Table A1. Summary of CO₂ adsorption capacities in terms of wt% CO₂/polymer, mmol CO₂/g polymer, or mol% CO₂/amidine for linear polymers and POPs as reported in literature.

Polymer/Matrix	CO ₂ -Adsorbing Group	Matrix Type	State	CO ₂ Adsorption			Ref
				wt% CO ₂ /polymer	mmol CO ₂ /g polymer	mol% CO ₂ /amidine	
Poly(VBTAm) ^a	N,N-dimethylacetamide	Linear Polymer	Solid	22	5.28		<i>This Work</i>
Poly(THPSt) ^b	1,4,5,6-tetrahydropyrimidine (THP)	Linear Polymer	Dissolved in DMF			73	Endo [50]
Poly(THPSt) ^b	1,4,5,6-tetrahydropyrimidine (THP)	Linear Polymer	Solid			12	Endo [50]
PVDMA ^b	1,4,5,6-tetrahydropyrimidine (THP)	Linear Polymer	Solid	~1	0.34	10-11	Barkakaty [57]
Poly(THPSt) + PEG ₄₀₀ ^b	1,4,5,6-tetrahydropyrimidine (THP)	Linear Polymer	Oil			45	Sakuragi [61]
Polyamidine ^b	Polyamidine	Linear Polymer	Solid			3.4	Furusho [54]
Polyamidine + PEG ₄₀₀ ^b	Polyamidine	Linear Polymer	Oil			66	Furusho [54]
P2DBN ^b	1,5-Diazabicyclo[4.3.0]non-5-ene	Linear Polymer	Solid			28	Ochiai [56]
Poly(ethyleneimine) ^b	Imine	Linear Polymer	Oil	0.30			Aschenbrenner [51]
PVBIT ^b	Imidazolium Salt	Linear Polymer	Solid	0.32	2.8		Tang [53]
[BIEMA][acetate] ^b	Imidazolium Salt	Linear Polymer	Solid	1.25			Privalova [52]
Benzimidazole-linked polymers (BILPs) ^c	Benzimidazole	POP	Solid	24	5.45		Rabbani [62]
Hexaazatriphenylene-based conjugated triazine framework (CTFs) ^b	Triazine	POP	Solid		4.8		Zhu [63]
Porous azo-linked polymers (ALPs) ^c	N/A	POP	Solid	5.37			Arab [64]
Poly(hydroxylindole)-NH ₂ aerogel ^c	Indole	POP	Solid	33			Xu [65]
Semi-cycloaliphatic polyimides (sPIs) ^c	Imide	POP	Solid	23.8			Yan [66]

Table A1. Continued.

Tertiary amine-functionalized porous organic polymer ^c	Tertiary amine	POP	Solid	85.8 ^d	19.5		Gomes [67]
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^aConditions = 27 °C, 1 bar, pure CO₂ flow. ^bConditions = 25 °C, 1 bar, pure CO₂ flow. ^cConditions = 0 °C, 1 bar, pure CO₂ flow. ^dAmong the highest values ever reported for POPs (known to date).

CHAPTER II
SYNTHETIC CHALLENGES IN THE THP-FUNCTIONALIZATION OF MONMERS
AND POLYMERS

2.1 Abstract

The monocyclic amidine, THP, is recognized for its ability to quantitatively capture and release CO₂ in solution, but previous researchers have struggled to incorporate THP moieties into polymers to create solid sorbets because the functionalized materials suffer from insolubility or undergo side reactions related to ring-opening of the THP by hydrolysis. Here, I describe several approaches to the synthesis of a soluble THP-functionalized copolymer. First, functionalization of the monomer 2-hydroxyethyl acrylate (2-HEA) was attempted by two synthetic approaches: 1) Mitsunobu reaction to facilitate condensation between THP and the terminal alcohol of 2-HEA and 2) nucleophilic attack of THP after tosylation of the alcohol group of 2-HEA. Both routes were unsuccessful due to a competing aza-Michael addition reaction at the α,β -unsaturated carbonyl group in 2-HEA. An alternate approach involving a KI-catalyzed reaction to substitute THP at the chlorinated site of 4-vinylbenzyl chloride (VBC) successfully yielded a THP-functionalized, styrene-based monomer, THPSt, when a ratio of THP:VBC = 4:1 was used. However, THPSt could not be polymerized by free radical polymerization. Therefore, RAFT copolymerization of styrene and VBC was followed by post-polymerization modification using a KI-catalyzed reaction to substitute THP at the chlorinated sites of the VBC repeat units, yielding the THP-functionalized copolymer poly(St-*ran*-THPSt). Although the VBC composition is controlled by the feed ratio in the RAFT copolymerization, post-polymerization modification did not achieve quantitative conversion, and the tendency of THP to hydrolyze (when exposed to slightly elevated temperatures and moisture) resulted in degradation of the polymer side chains and crosslinking reactions due to hydrogen bonding that resulted in an insoluble polymer network. The results of this work demonstrate the sensitivity of THP to side reactions and, by extension, contribute valuable knowledge to efforts to create THP-functionalized solid polymers for CO₂ capture/release.

2.2 Introduction

Amidines are usually researched because of their ability to capture and release carbon dioxide (CO_2) at ambient temperature and pressure, as shown by the reversible capture/release mechanism shown in Scheme 1.1. These reversible capture/release behaviors are based on chemical properties and structural factors such as basicity and steric hindrance, as well as environmental factors such as temperature and moisture. Several researchers have studied these behaviors in solution using various amidine derivatives. For instance, Yin et al. studied derivatives of melamine to establish a relationship between basicity and CO_2 adsorption.⁶⁸ They found that the ease of CO_2 capture and release is directly linked to the protonation and deprotonation of the amine groups in the melamine derivative, which in turn is related to the pK_a of the conjugate acid, pK_aH , of these groups. For example, the pK_aH of melamine derivatives increases with increasing degree of methylation on the exocyclic amines, indicating increased basicity. This trend is evident in the pK_a values of melamine (pK_aH 5.0), methylmelamine (pK_aH 5.3), and trimethylmelamine (pK_aH 5.8). The CO_2 adsorption capacity, correspondingly, increased from 18.6% for melamine, to 28.5% for methylamine, and to 50.0% for trimethylmelamine when these compounds were exposed to CO_2 that was bubbled through their aqueous solutions. This pattern demonstrates a relationship between basicity of the amine and CO_2 adsorption capacity.

Although amidines have greater nucleophilicity than amines and, therefore, generally exhibit greater CO_2 adsorption capacity,³⁴ they are prone to nucleophilic attack at electrophilic sites. This can often lead to alkylation of the amidine at both nitrogen centers, which disrupts their ability to adsorb CO_2 .^{69–75} For instance, Alici et al. reported that the cyclic amidine, MTHP, is quantitatively quaternized by 1,4-dibromobutane, which yields the di-functionalized salt, 3,3'-dimethyl-1,1'-buthylenedi(1,4,5,6-THP) dibromide.⁷⁵ The reaction occurs readily at room temperature in DMF

solvent, highlighting the ease with which both of the nitrogen centers on a monocyclic amidine can be alkylated. This behavior could result in undesirable intra- or inter-molecular crosslinking within THP-functionalized polymers, which would likely lead to insolubility. In addition, in environments with slightly elevated temperatures and moisture, amidines are susceptible to hydrolysis at the methine bridge, which degrades the amidine functionality and results in a loss of the ability to fix CO₂. Hydrolysis of a cyclic amidine results in ring-opening and results in the loss of the amidine moiety.^{76–82} For example, Perrin et al. reported that hydrolysis of 3,4,5,6-tetrahydropyridin-2-amine, a monocyclic amidine in which the C=N group is endocyclic and the primary amine is exocyclic, occurs by a nucleophilic attack of water at the methine bridge. The hydrolysis of this monocyclic amidine results in a hemiaminal intermediate that undergoes an elimination reaction to create a linear aminoamide. This degradation by hydrolysis was observed to be nearly complete (98% of the amidines were ring-opened).⁷⁸

In this chapter, we describe attempts to synthesize THP-functionalized monomers (and the corresponding copolymers) through four different reaction pathways: 1) alkylation of THP with 2-hydroxyethyl acrylate (2-HEA) using Mitsunobu reaction conditions, 2) tosylation of 2-HEA followed by nucleophilic attack by THP, 3) base-catalyzed (K₂CO₃ or KI) substitution reactions of THP onto 4-vinylbenzyl chloride and 4) post-polymerization modification by a KI-catalyzed substitution reaction.

The first reaction pathway, the Mitsunobu Reaction, has been demonstrated by previous researchers to condensate modestly acidic nitrogen-containing nucleophiles (similar to THP) with primary alcohols. For instance, Hirose et al. reported successful condensation between the moderately acidic p-toluenesulfonamide (pK_a 11.7) and phenylpropan-1-ol using Mitsunobu reaction conditions at room temperature, with a yield of 87% that was achieved within 24 h.⁸³

Mitsunobu reactions have also been successfully used for the condensation of alcohols with imidazole derivatives or the exocyclic nitrogen of heterocyclic amidines.^{84–86}

The second reaction pathway involved substitution of THP at a tosylated site on 2-HEA. This approach was inspired by Nunomoto et al., who reported that indole (pKa 17) salts experience competing C-alkylation (at the alpha or beta carbon) or N-alkylation depending on the leaving group on the alkyl chain and the participating metal in the indole salt.⁸⁷ The N-alkylated product, shown in **Figure 2.1**, is exclusively formed in reactions with potassium indole salts and -OTs as a leaving group on varying alkyl chains. They also found N-alkylation is heavily favored when using highly polar solvents (e.g. 30% DMF in THF).⁸⁷

The third reaction pathway, K₂CO₃ or KI catalyzed substitution reactions, was inspired by both Nunomoto et al. and Chen et al. Nunomoto described that KI-catalyzed substitution reactions almost exclusively yields the N-alkylated indole (97% yield), similar to the -OTs leaving group mentioned previously,⁸⁷ while Chen et al. described how K₂CO₃-catalyzed substitution reactions yield successful substitution of imidazole and imidazoline compounds at primary halides.⁸⁸ Finally, because of difficulties with these monomer syntheses, THP-functionalization on copolymers of styrene and VBC was carried out by post-polymerization modification using KI-catalyzed substitution of THP. Our attempts to synthesize THP-functionalized monomers contributes to understanding the reactivity of monocyclic amidines, their sensitivity to hydrolysis in environments with heat and moisture, and the solubility issues that result from hydrolysis in THP-functionalized polymer systems. These insights provide a foundation for future efforts to optimize amidine-containing solid sorbents for CO₂ adsorption.

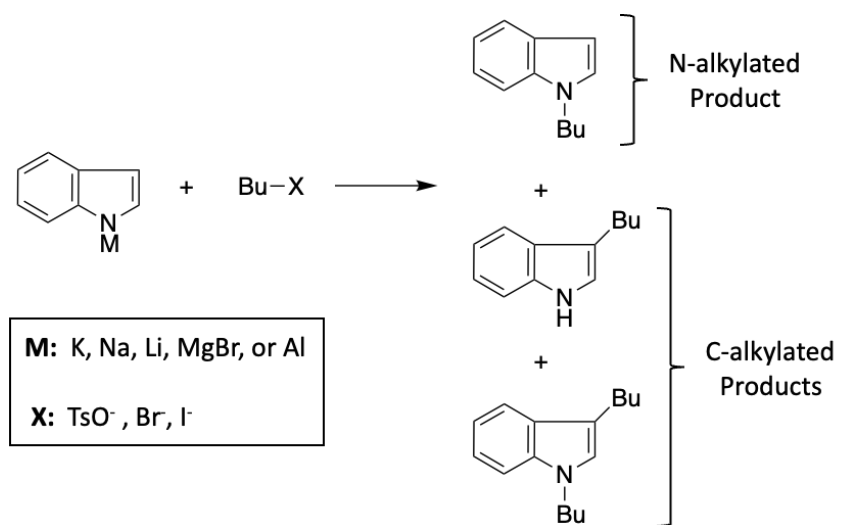


Figure 2.1. Alkylation of indole salts as reported by Nunomoto et al., where M is the participating metal in the indole salt, and X is the leaving group of the butyl group.⁸⁷

2.3 Materials and Characterization Methods

All reagents were used as received and all solvents were purchased as reagent-grade from Fisher Scientific unless stated otherwise. 2-hydroxyethylacrylate (2-HEA) was purchased from Fisher Scientific and dehydrated using a basic alumina column prior to any polymerization reactions. 1,4,5,6-tetrahydropyrimidine (THP) was purchased from Sigma Aldrich and used as received. 2,2'-Azobis(2-methylpropionitrile) (AIBN) was purchased from Sigma-Aldrich and recrystallized in methanol (MeOH) before use.

NMR spectra were collected on either a Varian Mercury Vx 300 MHz or a Varian VNMRs 500 MHz NMR at room temperature using either chloroform-*d* (CDCl₃) or methanol-*d*₄ (CD₃OD) solutions. The residual solvent peak served as an internal standard. High-resolution masses of small molecule products were measured using time-of-flight direct analysis in real time mass spectrometry (DART-MS). A JEOL AccuTOF DART mass spectrometer was used for these measurements. Samples were prepared at concentrations between 20 µg/mL and 1 mg/mL using toluene as the solvent. The standard peak voltage was between 600-800 V and the detector voltage was set to 2300 V. Number-average molecular weight (M_n) and dispersity ($\bar{D}$) were determined using an Agilent 1260 Infinity II GPC system using THF as the mobile phase at a flow rate of 1.0 mL/min. The system was equipped with a Wyatt Dawn Helios 8 multiangle light scattering detector and a Viscostar III and Optilab T-rEX detectors. Values of M_n and $\bar{D}$ were reported based on conventional calibration analysis using polystyrene standards. Samples were prepared in HPLC-grade THF at a concentration of 5 mg/mL and filtered through a 2.0 µm PTFE filter prior to injection. ATR-FTIR spectra were obtained using a Bruker Alpha II with a diamond crystal for ATR. Polymer samples were measured as dry solids using the platinum anvil. All small molecules were dissolved in toluene and deposited directly onto the ATR crystal without the use of the anvil.

The instrument resolution was 4 cm^{-1} and each sample was scanned for 16 scans to acquire its spectrum.

2.4 Synthetic approaches to THP-Functionalized Monomers

2.4.1 First Reaction Pathway – Mitsunobu Reaction

The general reaction scheme for the Mitsunobu reaction is presented in Scheme 2.1, in which an azo reagent and ligand are used to facilitate the condensation of THP with the terminal alcohol on 2-HEA. Several reagents and reaction parameters were adjusted to optimize the Mitsunobu Reaction and a list of reaction attempts is presented in **Table 2.1**. As an example, reaction 1b describes 2-hydroxyethyl acrylate (2-HEA) (58.06 mg, 0.5 mmol) dissolved in dimethylformamide (DMF) (2.5 mL) in a round bottom flask containing a stir bar. 1,4,5,6-tetrahydropyrimidine (THP) (50.82 mg, 0.6 mmol), diisopropyl azodicarboxylate (DIAD) (121.33 mg, 0.6 mmol), and triphenylphosphine (PPh_3) (157.37 mg, 0.6 mmol) were added and then the flask was sealed with a septum. After sparging with argon for 10 minutes, the septum was removed quickly and then reseated to allow a small amount of oxygen into the reaction vessel. The reaction was allowed to stir at room temperature for 3 h. After this time, CHCl_3 (2.5 mL) was added to the flask, and the resulting mixture was extracted with water ($10\text{ mL} \times 3$) and then brine ($10\text{ mL} \times 3$). The organic layers were collected and dried over magnesium sulfate (MgSO_4). Then, the solvent was removed by rotary evaporation at reduced pressure and then the concentrated product was separated by column chromatography using a mixture of DCM and

Scheme 2.1. General reaction scheme for the attempted Mitsunobu coupling of 2-HEA and THP.

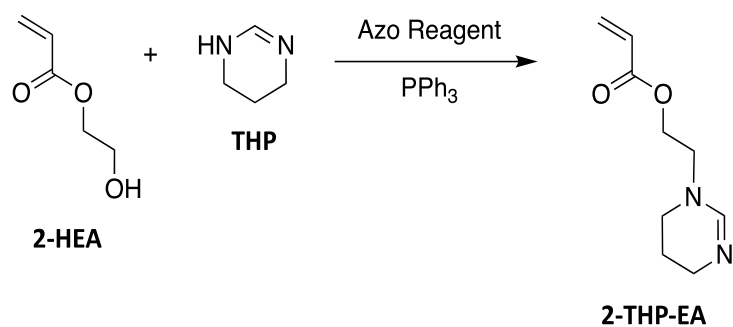


Table 2.1. Reaction conditions used for the Mitsunobu condensation of various alcohols with THP.

Reaction	Alcohol	Solvent	Azo Reagent	Temperature (°C)	Time (h)
1a	2-hydroxyethyl acrylate	THF	DIAD	r.t.	3
1b	2-hydroxyethyl acrylate	DMF	DIAD	r.t.	3
1c	1-butanol	DMF	DIAD	r.t.	3
1d	1-butanol	DMF	DIAD	70	3
1e	2-hydroxyethyl acrylate	DMF	DIAD	120	24
1f	1,8-octanediol	Toluene	ADDP	80	24
1g	2-hydroxyethyl acrylate	None	None	r.t.	18

MeOH (DCM:MeOH = 25:1 v/v) as the eluent on a silica gel column to yield the product. ^1H NMR spectroscopy and DART-MS were used to characterize the purified material.

2.4.2 Second Reaction Pathway – Tosylation Followed by Nucleophilic Attack

The general scheme for the second pathway, which involved tosylation of 2-HEA followed by THP functionalization is shown in Scheme 2.2. In a round bottom flask equipped with a stir bar, 2-HEA (1.16 g, 10 mmol) was dissolved in chloroform (20 mL) and the contents cooled to 0 °C. While stirring the solution, pyridine (1.19 mL, 15 mmol) was added followed by the addition of p-toluenesulfonyl chloride (1.91 g, 10 mmol) in small increments. The reaction mixture was stirred at room temperature for 3.5 h. After this time, diethyl ether (30 mL) and water (7 mL) were added to the reaction mixture, and the organic layer was washed with 2N HCl, 5% NaHCO_3 , and deionized water and then dried with MgSO_4 . The crude product mixture derived from the organic layers was concentrated by rotary evaporation and then isolated by column chromatography (2% ether/petroleum ether) on a silica gel column to yield the tosylated product, 2-(tosyloxy)ethyl acrylate (2-TEA), as a clear oil. The isolated 2-TEA was confirmed by ^1H NMR spectroscopy.

In order to facilitate THP-substitution at the tosyl group of site 2-TEA, various reaction parameters were adjusted and these reaction attempts are listed in **Table 2.2**. In a round bottom flask, 2-TEA (273.6 mg, 1.0 mmol) was dissolved in acetone (2 mL). THP (84 mg, 1.0 mmol) was added to the solution dropwise and the reaction was stirred at room temperature for 5 h. After this time, the solvent was removed by rotary evaporation to yield an orange oil.

Scheme 2.2. General reaction scheme tested for synthesis of THP-functionalized monomer, 2-TEA.

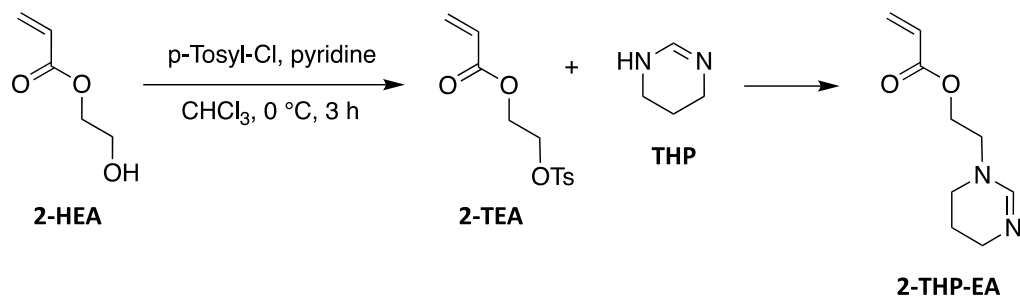


Table 2.2. Reaction conditions tested for THP-functionalization by $\text{S}_{\text{N}}2$ substitution on the tosylated monomer, 2-TEA.

Reaction	Solvent	Temperature ($^\circ\text{C}$)	Time (h)
2a	Acetone	35	5
2b	DMF	35	5
2c	Acetone	r.t.	24
2d	Acetone	r.t.	48
2e	Acetone	r.t.	0.75

2.4.3 Third Reaction Pathway – K₂CO₃-Catalyzed Nucleophilic Substitution

The general reaction scheme for the K₂CO₃-catalyzed THP-substitution reaction is shown in Scheme 2.3. Several reaction parameters were adjusted in an attempt to synthesize THPSt-HCl using K₂CO₃ as a base and these attempts are listed in **Table 2.3**, where reaction 3f is described here as an example. In a round bottom flask containing a stir bar, potassium carbonate (K₂CO₃) (0.830 g, 6.0 mmol) and VBC (0.306 g, 2.0 mmol) were dissolved in acetone (4 mL). THP (0.348 g, 3.0 mmol) was then slowly added while stirring and then the flask was sealed with a rubber septa. The reaction mixture was stirred for 18 h at 60 °C, the solvent was removed by rotary evaporation under reduced pressure. The resulting concentrate was dissolved in DCM (5 mL) and washed with a solution of 2M hydrochloric acid (HCl) (10 mL), deionized water (10 mL), then brine (10 mL), and dried with MgSO₄. The resulting crude product mixture was purified by column chromatography (5% MeOH in DCM) using a silica gel column. The final product was analyzed by ¹H NMR spectroscopy and DART-MS, which is reported and discussed in section 2.4.2.

2.4.4 Third Reaction Pathway – KI-catalyzed Nucleophilic Substitution

The general reaction scheme for the KI-catalyzed THP-substitution reaction is shown in Scheme 2.3. Several reaction parameters were adjusted in an attempt to synthesize THPSt-HCl using KI as a base and these attempts are listed in **Table 2.3**, where reaction **M** is described here as an example. To a round bottom flask containing a stir bar, potassium iodide (KI) (33.2 mg vinylbenzyl chloride (VBC) (76.31 mg, 0.5 mmol) was then added and the flask was capped with a rubber septa. The reaction mixture was then stirred at room temperature for 18 h. After this time, the solvent was removed by rotary evaporation under reduced pressure at 40 °C. The remaining concentrate was dissolved in CHCl₃ (15 mL) and washed with 2M HCl (15 mL),

Scheme 2.3. General synthesis for the K_2CO_3 -catalyzed substitution reaction, which yields the protonated THP-functionalized monomer, THPSt-HCl.

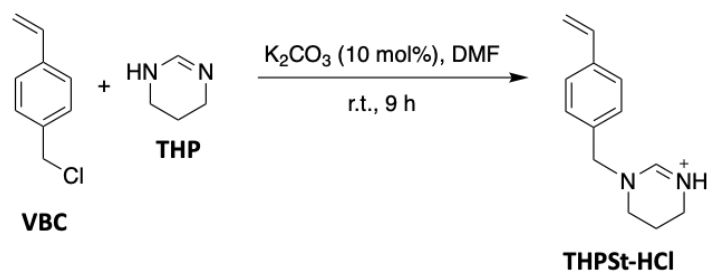


Table 2.3. Reaction conditions used for K_2CO_3 -catalyzed or KI-catalyzed nucleophilic substitution reactions for THP-functionalization at various halide sources.

Reaction	Halide Source	Base	Halide : THP : Base (mol ratio)	Solvent	Temperature (°C)	Time (h)
3a	VBC	K_2CO_3	2 : 3 : 6	DMF	60	18
3b	VBC	K_2CO_3	2 : 3 : 6	Acetone	60	18
3c	VBC	n/a	2 : 3 : 0	DMF	90 $\rightarrow$ r.t. ^a	18
3d	1-bromohexane	K_2CO_3	3 : 2 : 6	DMF	60	18
3e	1-bromohexane	K_2CO_3	3 : 2 : 6	Acetone	60	18
3f	Styrene	K_2CO_3	1 : 1 : 3	Acetone	60	18
3g	VBC	KI	1 : 1 : 0.1	Acetone/ THF	65	18
3h	Benzyl-Cl	KI	1 : 2.1 : 0.2	DMF	80	18
3i	Benzyl-Cl	KI	1 : 1.1 : 0.1	DMF	r.t.	18
3j	Benzyl-Cl	KI	1 : 1.1 : 0.1	DMF	40	18
3k	Benzyl-Cl	KI	1 : 1.1 : 0.1	DMF	60	18
3l	Benzyl-Cl	KI	1 : 4.2 : 0.4	DMF	r.t.	18
3m	VBC	KI	1 : 4.2 : 0.4	DMF	r.t.	18

^aReaction 3c was stirred for 8 h at 90 °C and then cooled to room temperature to stir for another 12 h .

0.21

mmol) and THP (0.177 g, 2.1 mmol) were added and dissolved with DMF (15 mL). 4- deionized water (20 mL) and brine (20 mL), and then dried with MgSO_4 . The crude product was then purified by column chromatography (1.5% MeOH in a solution of DCM : Acetone = 4:1) using a neutral alumina column. The product was isolated as a clear oil and the structure confirmed by ^1H NMR spectroscopy and DART-MS, which is reported and discussed in section 2.4.2.

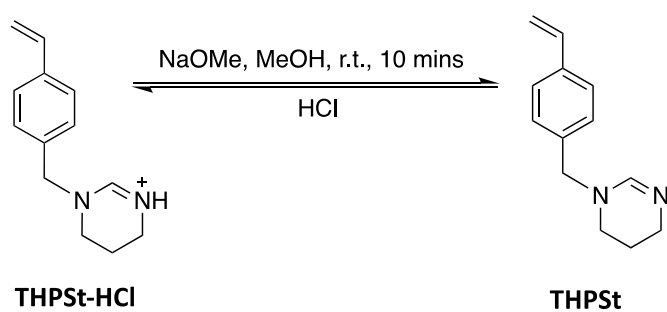
2.4.5 Deprotonation of THPSt-HCl

Having successfully synthesized THPSt-HCl, it was necessary to deprotonate it in order to obtain the neutral amidine motif that is capable of CO_2 capture. For this, a procedure similar to that described by Sakuragi et al. (Scheme 2.3) was used.⁶¹ Specifically, a round bottom flask containing a stir bar and 0.2 M solution (5 mL) of THPSt-HCl in MeOH was capped with a rubber septa and sparged with argon for 5 mins. After this time, a syringe was used to slowly add a 0.1 M solution (10 mL) of sodium methoxide (NaOMe) in MeOH to the reaction flask, and the reaction mixture was allowed to stir for 10 minutes at room temperature while continuing to sparge with argon. The solvent was then removed by rotary evaporation and the remaining concentrate was dissolved in CHCl_3 and filtered to removed insoluble particles. The solvent was removed under reduced pressure to yield the product as a clear oil. The structure was confirmed by ^1H NMR spectroscopy, which is reported and discussed in section 2.4.2.

2.4.6 Protonation of THPSt – Using HCl in Diethyl Ether

In a modified procedure by Endo et al. (Scheme 2.3),⁵⁰ THPSt was dissolved in a small amount of CHCl_3 and then poured into an excess amount of diethyl ether at a volumetric ratio of 3:500, respectively. After the solids were removed by filtration, 2M HCl in diethyl ether (18 mL) was added dropwise to the filtrate, which was in an ice bath at 0 °C. The precipitate was collected by vacuum filtration and purified by column chromatography using 8% MeOH in a

Scheme 2.3. General synthesis for the deprotonation of THPSt-HCl and the reverse reaction to protonate THPSt.



mixture of DCM and Acetone at a volumetric ratio of 4:1 DCM:Acetone as the eluent on a neutral alumina column. The desired isolated product THPSt-HCl was confirmed by ^1H NMR spectroscopy.

2.4.7 Protonation of THPSt – HCl Gas Bubbling

An alternate method to protonate THPSt involving generation of HCl gas by adding concentrated H_2SO_4 dropwise to solid sodium chloride (NaCl) as shown in Scheme 2.5. The HCl gas that was produced was bubbled into a stirred solution of the crude THPSt (6.17 g) dissolved in 1000 mL of diethyl ether until the solution appeared to be saturated with a suspension of white solids. The excess HCl gas was bubbled through a dilute solution of NaOH, and the pH of that solution was tested to ensure it had a neutral pH before disposal. The precipitate was collected by vacuum filtration and purified by column chromatography using 8% MeOH in a mixture of DCM and acetone (DCM:Acetone = 4:1) as the eluent on a neutral alumina column. The isolated product THPSt-HCl was confirmed by ^1H NMR spectroscopy.

2.5 Synthetic approaches to THP-Functionalized Polymers

2.5.1 Polymerization of THPSt-HCl

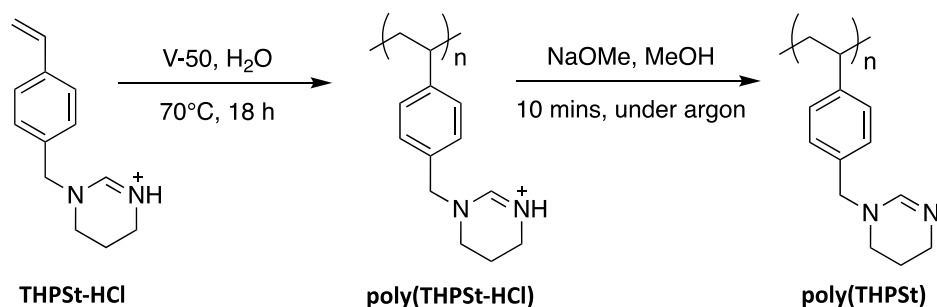
Following a procedure similar to that described by Sakuragi et al. (Scheme 2.5),⁶¹ 2,2'-azobis(2-methylpropionamidine) dihydrochloride (V-50) (0.157 g, 0.58 mmol) and THPSt-HCl (1.164, 5.8 mmol) were added to a round bottom flask containing deionized water (4.5 mL). The reaction flask was capped with a septum and the mixture was sparged with argon for 15 minutes at room temperature before the flask was placed in an oil bath preheated to 70 °C. The reaction was allowed to proceed for 18 h while the mixture was stirred. After this time, the reaction was quenched by freezing with liquid nitrogen. After the contents thawed, the crude product mixture

was precipitated into THF. The solids were collected, redissolved in MeOH, and precipitated 4 more times in diethyl ether. The isolated product was obtained as a yellow powder and characterized by ^1H NMR spectroscopy.

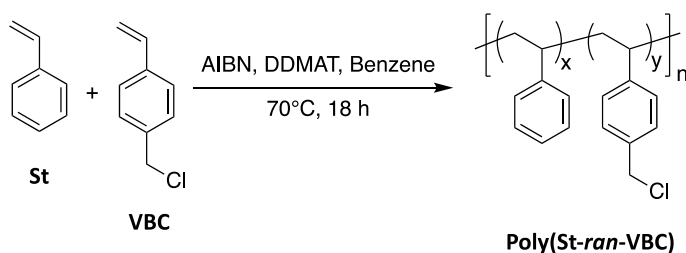
2.5.2 Reversible Addition-Fragmentation Chain Transfer (RAFT) Random Copolymerization of Styrene and VBC

Random copolymers of styrene (St) and vinyl benzyl chloride (VBC) were synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization as shown in Scheme 2.6. As an example, the preparation of a poly(St-*ran*-VBC) with an equimolar feed ratio of comonomers is described here. Styrene (0.710 g, 6.81 mmol) and VBC (1.04 g, 6.81 mmol) were added to a 5 mL round bottom flask containing AIBN (2.33 mg, 0.0141 mmol) and 2- (dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT) (25.9 mg, 0.0710 mmol) that was pre-dissolved in dry anisole (0.933 mL). The flask was sealed with a septum and contents were sparged with argon for 20 min. Then the flask was lowered into

Scheme 2.4. Free radical polymerization of THPSt-HCl and subsequent deprotonation.



Scheme 2.5. Random Copolymerization of styrene and VBC by Reversible Addition-Fragmentation Chain Transfer Polymerization.



the oil

a bath preheated to 70°C and allowed to react for 18 h while stirring. After this time, the reaction was quenched by immersing the flask in liquid nitrogen until the contents completely froze. After thawing, the solution was diluted with THF and then precipitated into hexanes. The solids were collected by gravity filtration and then redissolved in THF. This redissolution/precipitation cycle was performed a total of three times to yield a fluffy yellow powder. The solid copolymer was dried at 30 °C overnight under vacuum to yield a yellow powder. The polymer was characterized by ^1H NMR spectroscopy and gel permeation chromatography (GPC). The number-average molecular weight determined by GPC relative to polystyrene standards was $M_n = 10,800$ g/mol and the dispersity $\bar{D} = 1.11$. (GPC trace is shown in **Figure B1**.) Molar composition was determined via ^1H NMR to be 56 mol% VBC,

as assessed from the benzylic methylene at 4.51 ppm and aromatic protons ranging from 6.20-7.24 ppm. (See **Figure B2**.)

2.5.3 Fourth Reaction Pathway - Post-Polymerization Modification by KI-catalyzed Substitution

The procedure for the post-polymerization modification of poly(St-*ran*-VBC) to install pendant THP groups is described here using an example in which the molar composition of VBC in the copolymer is 47%. The Finkelstein reaction was carried out similar to the procedure reported in section 2.4.4, as shown in Scheme 2.7. Briefly, a pre-made solution of poly(St-*ran*-VBC) (0.250 g, 1.40 mmol -Cl) in DMF (5 mL) was added dropwise to a round bottom flask containing a stirring solution of potassium iodide (KI) (97.6 mg, 0.59 mmol), THP (0.495 g, 5.88 mmol), and DMF (5 mL). The reaction was allowed to stir at room temperature for 18h. After this time, the reaction mixture was precipitated into cold acetone. The resulting polymer is a protonated THP-functionalized copolymer, which was analyzed by ¹H NMR spectroscopy (shown in **B3**).

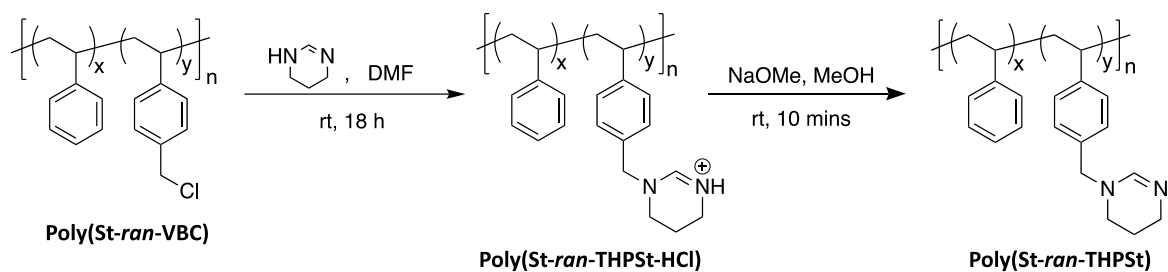
The protonated copolymer was then deprotonated by a procedure similar to the deprotonation of THPSt-HCl in section 2.4.5. In a round bottom flask containing a stir bar, a solution of the protonated copolymer (0.250 g, 1.40 mmol -THP), containing 47% THP-functionalization, in methanol (10 mL) was created. The flask was capped with a rubber septa and sparged with argon for 5 mins. After this time, a 0.1 M solution of NaOMe (10 mL) was added dropwise to the solution while stirring and continuing to sparge. The reaction was allowed to proceed for 10 mins, after which time the reaction solution was precipitated into diethyl ether. The solvent was decanted off to isolate the copolymer solids, which was reconstituted in methanol. The precipitation/reconstitution procedure was repeated a total of three times. The collected copolymer

solids were then dried under vacuum at room temperature overnight. The copolymer was analyzed by ^1H NMR spectroscopy for characterization.

2.6 Results and Discussion

The synthesis of 2-(5,6-dihydropyrimidin-1(4H)-yl)ethyl acrylate (2-THP-EA) was attempted by two different synthetic approaches: 1) The Mitsunobu reaction and 2) tosylation followed by nucleophilic substitution. Both of these approaches attempt to add THP functionality to the hydroxyl group of 2-HEA. However, in both synthetic approaches, THP preferred an aza-Michael addition at the α,β -unsaturated carbonyl group of 2-HEA. This is not surprising, since similar aza-Michael additions of 1,4-conjugates have been well documented.^{89–96} To eliminate the aza-Michael addition side reaction, THP-functionalization of a styrene-based monomer, VBC, was pursued in a two-step process involving a base-catalyzed (K_2CO_3 or KI) substitution reaction that was

Scheme 2.6. Post-polymerization modification route for the synthesis of poly(St-*ran*-THPSt). A Finkelstein reaction was performed on poly(St-*ran*-VBC) followed by deprotonation to yield the neutral copolymer.



followed by deprotonation. Although successful, the resulting THPSt monomer could not be polymerized by any free radical polymerization technique. To circumvent this issue, random copolymers of styrene and VBC were prepared by RAFT polymerization, followed by a post-polymerization modification route employing KI-catalyzed substitution of THP at the benzyl chloride sites. However, this pathway suffered its own challenges, including incomplete conversion of benzyl chlorides (THP-functionalization) as well as side reactions that resulted in degradation of THP motifs. This section highlights several challenges associated with monomer and copolymer functionalization using the cyclic amidine moiety, THP.

2.6.1 Attempted Synthesis of 2-THP-EA

2.6.1.1 First Reaction Pathway – Mitsunobu Reaction.

Many modifications to the Mitsunobu reaction conditions were made in an attempt to perform a condensation between THP and the hydroxyl group of 2-HEA. The general scheme is presented in Scheme 2.1 and examples of attempted reaction conditions can be found in **Table 2.1**. Unfortunately, THP shows a preference for an aza-Michael addition at the α,β -unsaturated carbonyl, as depicted in Scheme 2.8. This preference is supported by the disappearance of the α and β protons (**a** and **b**) in the black (top) ^1H NMR spectrum presented in **Figure 2.1**. Additionally, the **c'** and **d'** methylene protons only exhibit only a minor shift compared to the **c** and **d** protons of the starting material, 2-HEA, shown in the red spectrum. This minor shift strongly suggests that the reaction had a minimal effect on the electron density around these protons (no change in shielding), indicating that THP likely did not react at the hydroxyl site. To probe the reactivity of THP and 2-HEA, THP and 2-HEA were reacted in stoichiometric proportion in the absence of solvent and azo reagent, as described by reaction 1g in **Table 2.1**.

Scheme 2.7. The proposed aza-Michael Addition that occurs in a neat reaction between 2-HEA and THP.

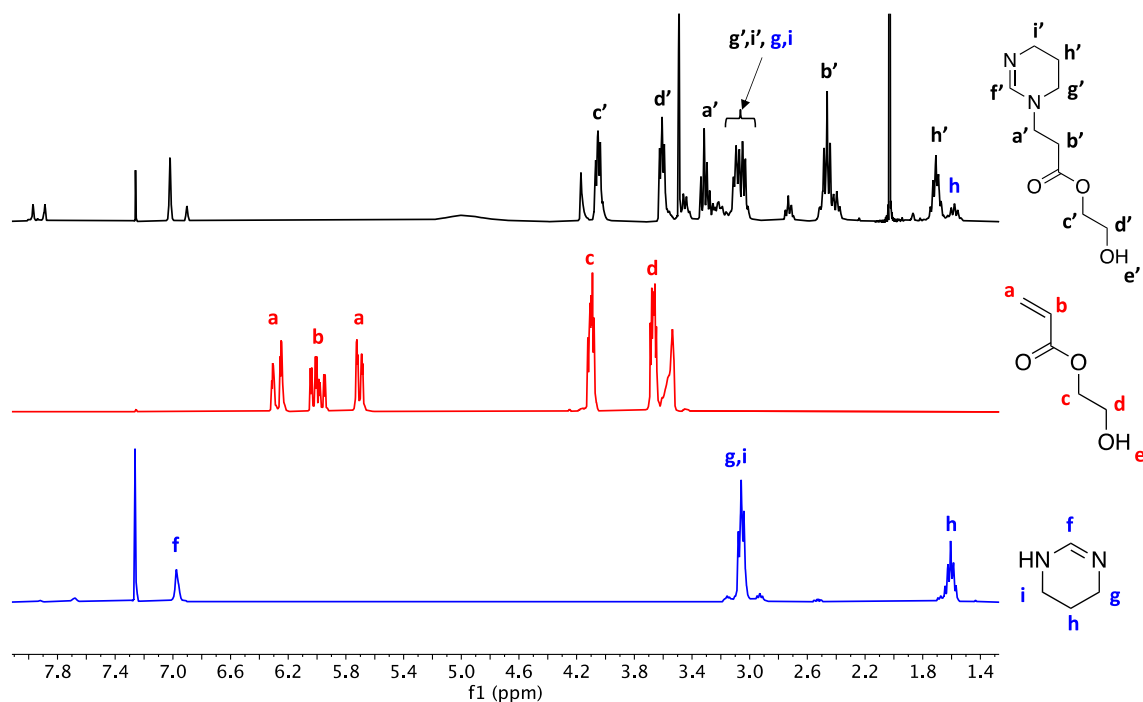
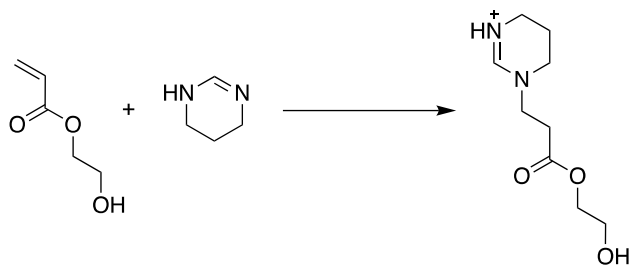


Figure 2.2. Stacked ¹H NMR spectra of the attempted condensation of 2-HEA (red) and THP (blue) using Mitsunobu conditions (reaction 1e, Table 2.1). The black spectrum is the resulting reaction mixture that contains indications of the aza-Michael Addition product, notably by the disappearance of peaks **a** and **b**. ¹H NMR (300 MHz, 25°C, CDCl₃).

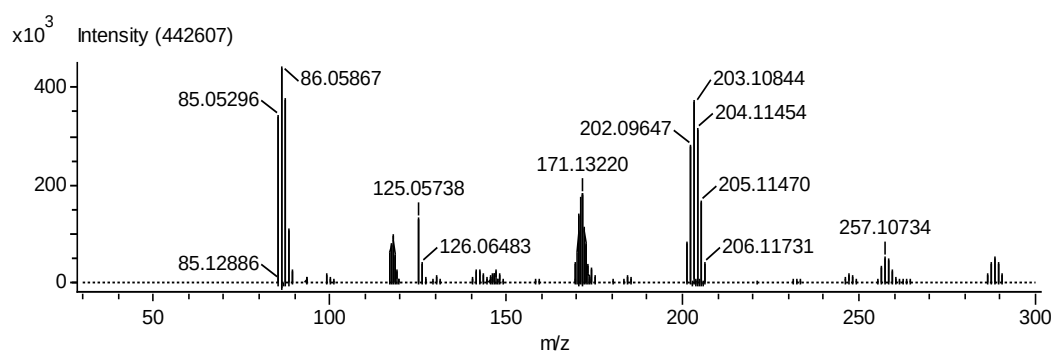


Figure. 2.3. DART-MS in positive ion mode for the attempted Mitsunobu Reaction yielding multiple side products.

Mitsunobu reaction resulted in formation of an aza-Michael addition product instead of the desired product resulting from condensation of THP at the hydroxyl of 2-HEA.

In an attempt to assess the feasibility of Mitsunobu coupling of THP with a primary hydroxyl group, I chose 1,8-octanediol as the model primary alcohol and changed the azo compound from DIAD to 1,1'-(azodicarbonyl)dipiperidine (ADDP). This attempt is reported by reaction 1f in **Table 2.1**. The use of 1,8-octanediol eliminates the possibility of aza-Michael Addition side product. Furthermore, to improve the reactivity of THP, the azo compound, DIAD, was substituted with ADDP. ADDP is known to enhance the reactivity of nucleophiles with pKa values between 11 and 13, which aligns closely with the pKa of THP, approximately 12.8 to 13.⁶⁹ The reaction product was analyzed by ¹H NMR as shown by the black spectrum in **Figure 2.4**. However, the spectrum shows a significant amount of 1,8-octanediol remaining in the crude reaction as indicated by the protons labelled **a**, **b**, and **c** from the red spectrum that still remain in the product mixture (black spectrum). This is due to the reaction stoichiometry being set such that there are twice as many hydroxyl groups compared to THP units, resulting in complete exhaustion of the THP starting material as indicated by the absence of the **g** and **e** protons (from the blue spectrum) in the product mixture (black spectrum). Therefore, the interpretation of the ¹H NMR spectra suggests successful alkylation of THP. The **d** proton, assigned to the methine proton on THP, has likely shifted downfield, which is behavior that would be consistent with successful alkylation of the amidine (discussed further in section 2.4.2). However, the shifted signal would overlap with the PPh₃ signals in the aromatic region. The crude reaction material was also characterized by DART-MS and the resulting spectrum is shown in **Figure 2.5**.

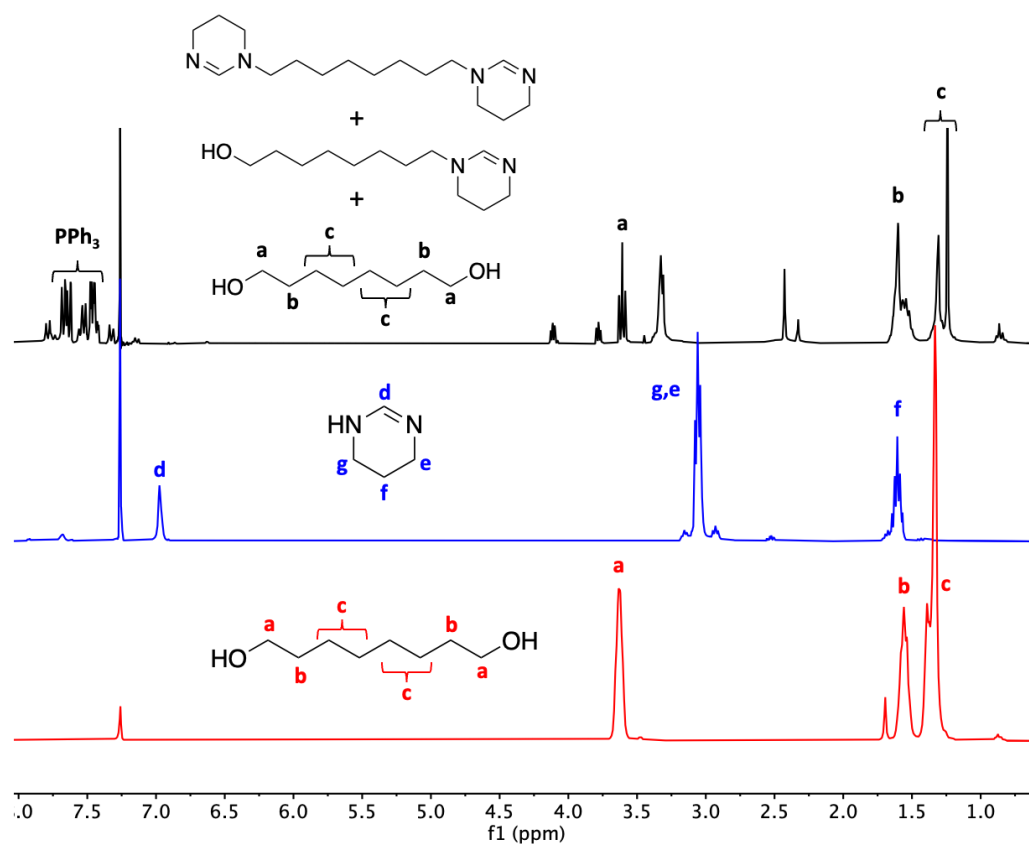


Figure 2.4. Stacked ^1H NMR showing the attempted Mitsunobu Reaction product (entry 1f, Table 2.1) (black spectrum) resulting from coupling 1,8-octanediol (red spectrum) with THP (blue spectrum). ^1H NMR (300 MHz, 25°C , CDCl_3).

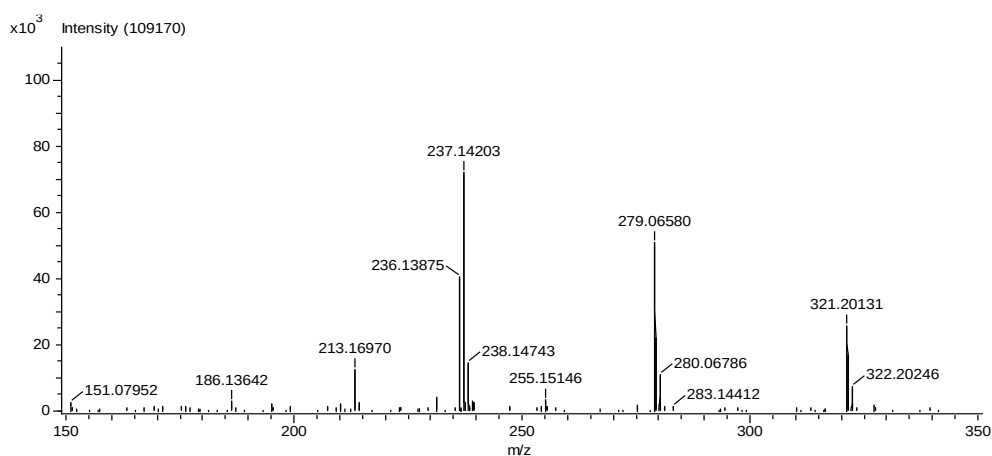


Figure 2.5. DART-MS spectrum acquired in positive ion mode for the resulting product of the Mitsunobu reaction of 1,8-octanediol and THP. A mixture of the mono- and di-functionalized products, along with other reaction impurities, are present. The mono-functionalized product is represented by the signal at $m/z = 213.1697$ (calc'd $[M+H]^+ = 213.2011$) and the di-functionalized product is represented by the signal at $m/z = 279.0658$ (calc'd $[M+H]^+ = 279.2541$).

The presence of a peak at $[M+H^+] = 213.1697$ corresponds with the calculated mass of the mono-functionalized target molecule, $[M+H^+]_{\text{calc'd}} = 213.2011$, indicating a single, successful coupling of the 1,8-octanediol and THP. The major peak at $[M+H^+] = 279.0658$ corresponds to the calculated mass of the di-functionalized product, $[M+H^+]_{\text{calc'd}} = 279.2541$ that is consistent with having amidines having coupled at both terminal hydroxyls (the 1- and 8- positions). In hindsight, a slight molar excess of THP relative to hydroxyl groups could have reduced or eliminated the amount of mono-functionalized product formed. This test reaction strongly suggests that the Mitsunobu reaction can feasibly couple THP with primary alcohols. However, even with the usage of the more active ADDP azo reagent, it remains untested whether this reaction will favor condensation at the alcohol instead of the aza-Michael addition that takes place in the presence of an α,β -unsaturated carbon group.

A potential improvement in coupling efficiency could involve choosing a more suitable ligand to replace triphenylphosphine (PPh_3). Instead, PBu_3 is often chosen as the ligand for Mitsunobu reactions using ADDP, as described in a report by Hirose et al.⁸³ As shown on the left in **Figure 2.6**, PPh_3 , which is more sterically hindered compared to PBu_3 , is normally chosen to prevent formation of the hydrazine byproduct that occurs by unwanted alkylation of the azo reagent. However, since ADDP is already sterically hindered, hydrazine formation is unfavored. Therefore, using PBu_3 creates a less sterically hindered environment for the nucleophile (THP) to attack the substrate (the phosphine oxide formed at the hydroxyl) during the condensation, which is necessary for bulkier compounds such as THP. This effect of steric demand can be seen in **Figure 2.6**, and this suggests using ADDP/ PBu_3 as opposed to the DIAD/ PPh_3 may benefit the Mitsunobu coupling involving THP as the nucleophile.

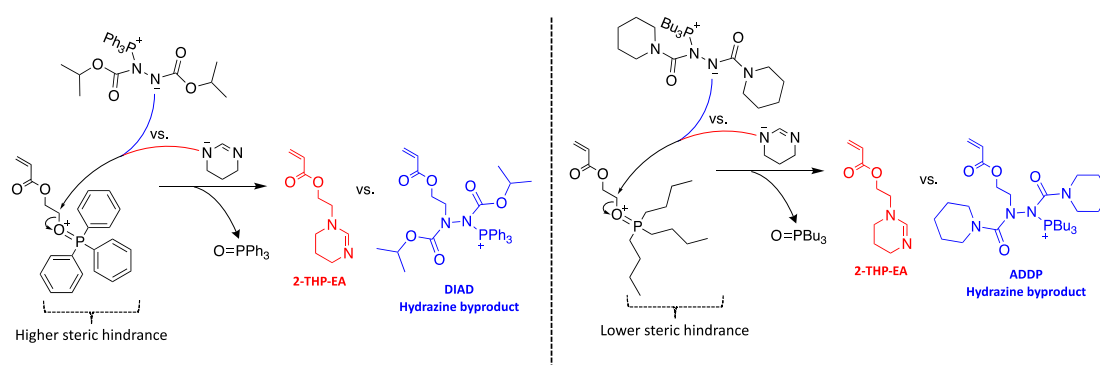


Figure 2.6. Partial mechanism of the Mitsunobu reaction illustrating the nucleophilic competition between the nucleophile (THP) and the azo reagent (DIAD or ADDP). Nucleophilic attack by THP results in the target product, 2-THP-EA, while nucleophilic attack by the deprotonated azo reagent results in the corresponding hydrazine byproduct. The mechanism also illustrates the degree of steric hindrance on the azo reagent/ligand pairing controls the degree of hydrazine byproduct formation.

the competing aza-Michael addition reaction that occurs in the presence of α,β -unsaturated carbonyl groups, the test reaction between THP and 1,8-octanediol strongly suggests that alkylation of the THP by the Mitsunobu reaction is feasible. In addition, it is possible that pairing the PBU_3 ligand with the ADDP azo reagent would provide better conditions for alkylation of THP at the hydroxyl group of 2-HEA. However, it remains untested whether or not the Mitsunobu reaction would be favored over the aza-Michael addition, even with ADDP and PBU_3 as the azo compound and ligand.

2.6.1.2 Second Reaction Pathway – Nucleophilic Attack on Tosylated 2-HEA.

The next attempt to synthesize the desired amidine-functionalized monomer, 2-THP-EA, involved a two-step method where 2-HEA was tosylated at the hydroxyl end group and followed by a substitution reaction using THP as the nucleophile. The tosylation step was successful and the ^1H NMR spectrum of the purified tosylated monomer, which is referred to as 2-TEA, is shown in Figure 2.7. Unfortunately, subsequent THP substitution was unsuccessful due to the preference for aza-Michael addition at the α,β -unsaturated carbonyl group of 2-HEA. This product mixture is shown by the black ^1H NMR spectrum in Figure 2.8. Although the product mixture was not purified, the disappearance of the α,β -unsaturated protons (a_1 , a_2 , b) is evident when comparing the product mixture (black spectrum) and 2-TEA starting material (red spectrum). The disappearance of the α,β -unsaturated protons in the ^1H NMR spectrum was also seen in Figure 2.1 for the Mitsunobu Reaction attempt reported by reaction 1e in Table 2.1, suggesting reactivity at the α,β -unsaturated carbonyl group of 2-HEA. DART-MS then confirmed the presence of the aza-Michael addition side product as shown in **Figure 2.2**. This behavior suggests that the attempted substitution at the tosylated site of 2-TEA also results

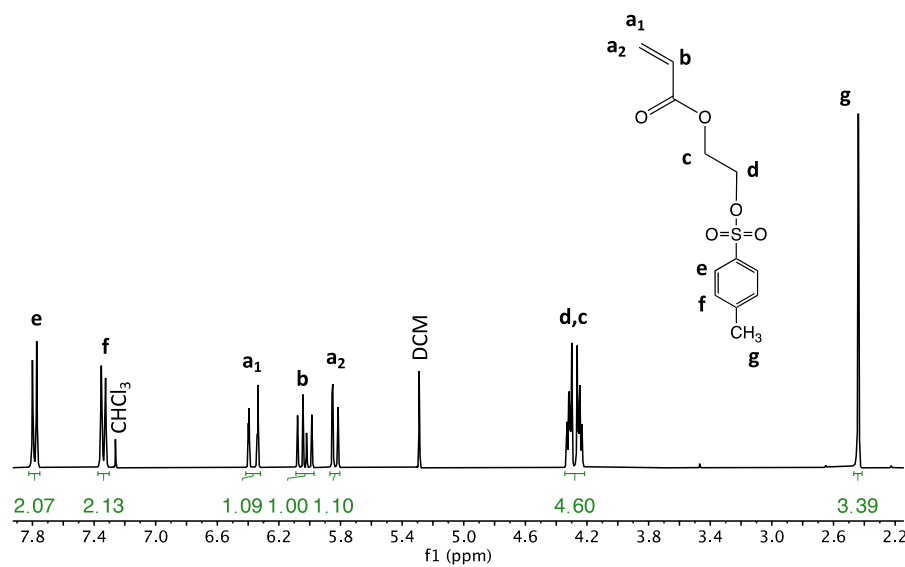


Figure 2.7. ^1H NMR for the isolated product resulting from tosylation of 2-HEA. ^1H NMR (300 MHz, 25°C, CDCl_3). δ , ppm: 2.44 (s, 3H, CH_3), 4.20–4.35 (m, 4H, CH_2), 5.80–5.87 (d, 1H, CH), 5.95–6.10 (q, 1H, CH), 6.30–6.43 (d, 1H, CH), 7.30–7.38 (d, 1H, arom. CH), 7.75–7.83 (d, 1H, arom. CH).

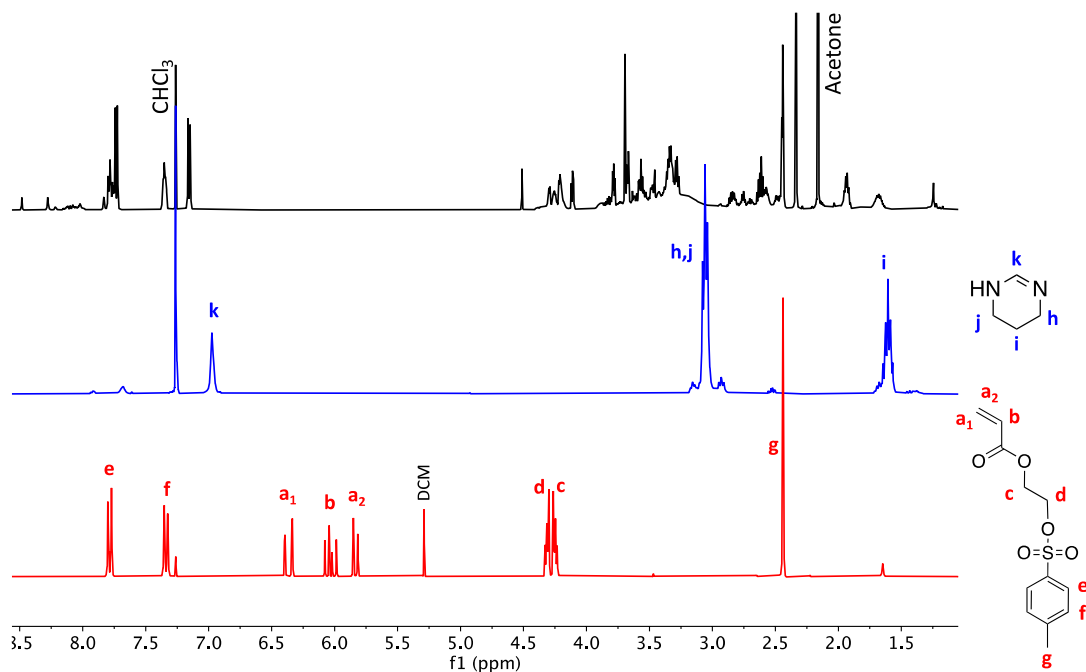


Figure 2.8. Stacked ^1H NMR spectra showing the product mixture (black) for the attempt to substitute THP at the tosylated site of 2-TEA. The blue spectrum identifies the proton shifts for THP and the red spectrum identifies the protons shifts for 2-TEA.

- in an

unwanted aza-Michael addition side reaction. However, the product mixture (black spectrum) does show upfield shifts of the aromatic protons, **e** and **f**, and the methyl proton, **g**, assigned to the tosyl group of 2-TEA. These upfield shifts could be attributed to the formation of p-toluenesulfonic acid (p-TsOH) – this would be a byproduct of THP substitution at the tosylated site. It is initially puzzling that protons **e**, **f**, and **g** appear more upfield for p-TsOH compared to protons of the tosyl group on the functionalized monomer, 2-TEA. Although the methylene protons, **c** and **d**, are considered electron donating groups by induction (which would shift the **e**, **f**, and **g** protons more upfield), the electron withdrawing nature of the methacrylate could induce a stronger deshielding effect. This could cause the 2-TEA protons to appear more downfield compared to the p-TsOH protons. While the substitution of THP at the tosylated site of 2-TEA was partially successful, there was still a strong preference of aza-Michael addition side products. Reports by Nunomoto et al. described successful N-alkylation of indoles ($\text{pK}_a \sim 17$) using a tosyl leaving group, however, the indoles were first deprotonated and made into salts having a potassium counterion.⁸⁷ Therefore, deprotonation of the THP moiety ($\text{pK}_a = 12.8\text{--}13.0$) prior to substitution could lead to successful N-alkylation of THP; however, competition for nucleophilic attack at the α,β -unsaturated carbonyl may remain an issue.

The aza-Michael addition, which is problematic because it competes with substitution, could be avoided by first polymerizing 2-TEA and then attempting the $\text{S}_{\text{N}}2$ substitution in a post-polymerization modification. This would strategy would eliminate the reactive α,β -unsaturated carbon group. However, incomplete conversion or the formation of side products would result in unwanted functionality on the polymer chain. A discussion on the synthesis, characterization, and challenges of post-polymerization modification products will be discussed later in detail in section 2.4.3.

2.6.2 Synthesis of THP-Functionalized Styrene-Based Monomer (THPSt)

Several attempts to optimize the base-catalyzed substitution reaction between THP and VBC were made involving changing solvent type, base catalyst, and reaction temperature before it became apparent that the dominant factor that controlled side product formation was the stoichiometric ratio between benzyl chloride groups and THP. Several of the attempted reaction conditions, which are captured in **Table 2.3**, will be discussed here in detail to explain this phenomenon.

2.6.2.1 Third Reaction Pathway – K_2CO_3 -Catalyzed Nucleophilic Substitution.

Initial attempts to synthesize THPSt used K_2CO_3 as a base catalyst to promote the substitution reaction. As an example, reaction 3a in **Table 2.3** used a molar ratio of VBC:THP = 2:3, which resulted in several side products, as shown by the ^1H NMR spectrum shown by the black trace in **Figure 2.9**. The clusters of proton shifts, labelled by the brackets in the black spectrum, strongly indicate that the side products do not change drastically in bond connectivity compared to the VBC and THP starting materials. For instance, the partial spectrum inset in **Figure 2.9**, which emphasizes the **b'** cluster, shows the presence of at least three sets of quartets, which indicates the presence of at least three different vinyl groups. Similarly, the VBC methylene proton, **d**, in the blue spectrum seems to result in five different methylene proton shifts in the range of 3.5 - 5.0 ppm for the product mixture (black spectrum).

2.6.2.2 Fourth Reaction Pathway – KI-Catalyzed Nucleophilic Substitution (Finkelstein Reaction).

In an attempt to avoid these side reactions, a Finkelstein reaction, which is a KI-catalyzed substitution reaction was attempted. Other works have demonstrated successful substitution

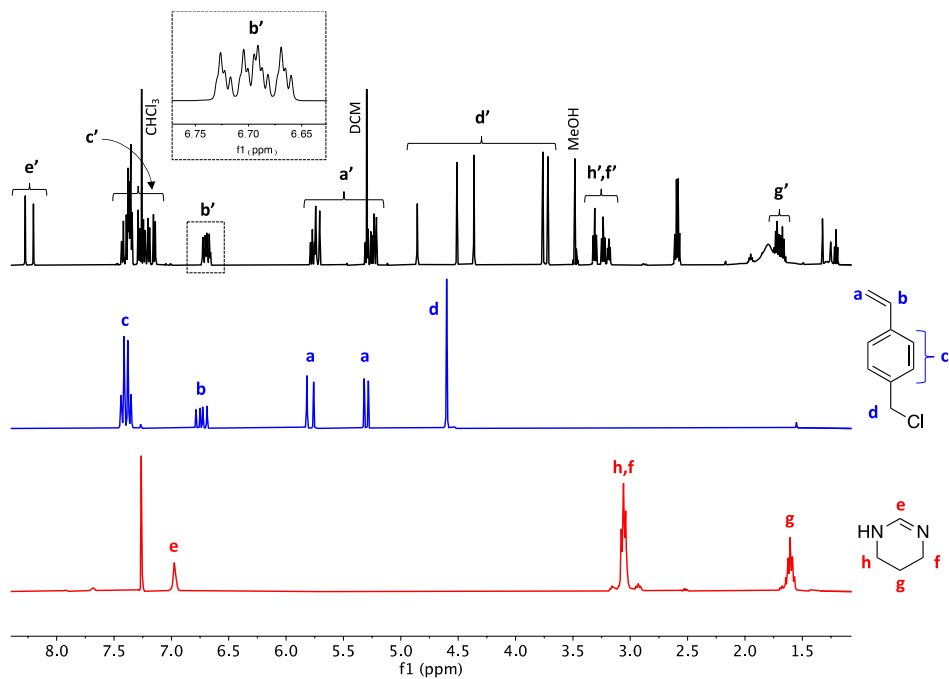
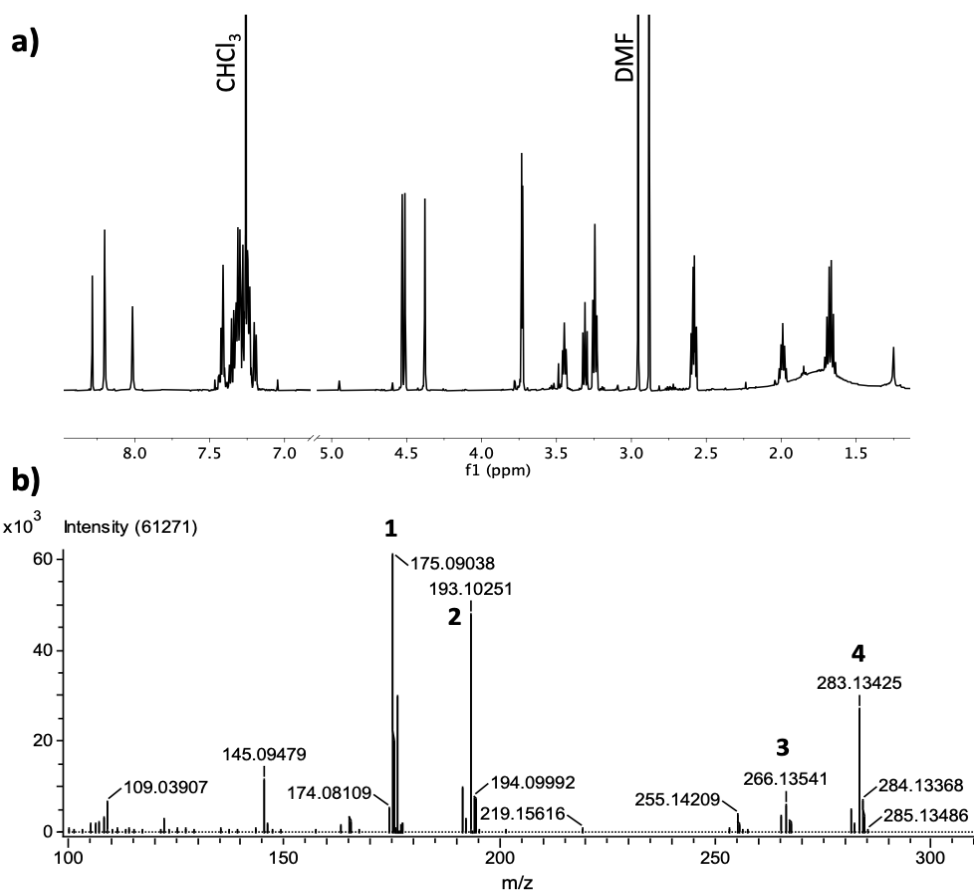


Figure 2.9. Stacked ¹H NMR spectra showing the product of the K₂CO₃-catalyzed substitution reaction (black spectrum) and the starting materials VBC (blue spectrum) and THP (red spectrum). ¹H NMR (500 MHz, 25°C, CDCl₃).

reactions where the secondary amines or cyclic imides act as the nucleophile and are substituted at primary halide centers or benzylic halides centers, resulting in good yields.⁸⁷ To avoid potential side reactions at the vinyl group of styrene, benzyl chloride was used to test the efficacy of the Finkelstein reaction, as reflected in reaction 3k in **Table 2.3**. The resulting ¹H NMR spectrum (**Figure 2.10a**) showed a “clustering” of proton shifts similar to the ¹H NMR product mixture (**Figure 2.8**) for the K₂CO₃-catalyzed reaction. Characterization by DART-MS indicated the presence of four major products, which are seen at m/z = 175.0904, 193.1025, 266.1354, and 283.1343 as shown in **Figure 2.10b**. The first reported mass, [M+H⁺] = 175.0904, matches the calculated mass of the target molecule, 1-benzyl-1,4,5,6-tetrahydropyrimidine (1-benzyl-THP-HCl, compound **1** in **Figure 2.10**), [M+H⁺]_{calc'd} = 175.1231. The difference in mass between peaks at [M+H⁺] = 175.0904 and 193.1025 is equal to the molecular weight of water. This strongly suggests that the second peak is the result of hydrolysis of compound **1**, yielding the ring-opened products depicted by compounds **2a** and **2b** in **Figure 2.10**. This is not surprising, as several reports have documented the hydrolysis of cyclic amidines when they are exposed to heat and moisture, even at low levels.^{76–81,97–101} The third species represented in the DART-MS spectrum, which is observed at [M+H⁺] = 266.1354, agrees with the calculated mass of THP after being alkylated at both nitrogen centers (by reaction with two benzyl halides) to yield 1,3-dibenzyl-3,4,5,6-tetrahydropyrimidin-1-ium (1,3-dibenzyl-THP), which is shown as compound **3** in **Figure 2.9**. This double substitution in which one THP can react with two benzyl chlorides is well-documented for monocyclic amidines.^{69–75,102} Similar to what was observed for compound **1**, the hydrolysis of compound **3** results in compound **4**, which has a mass [M+H⁺] = 283.1343.



	1	2a	2b	3	4
Structure					
[M+H⁺]_{calc}	175.1231	193.1337		266.1777	283.1805

Figure 2.10. ¹H NMR spectrum (**a**) and DART-MS spectrum (**b**) of the 1-benzyl-THP-HCl (**1**) and its ring-opened products (**2a** and **2b**), as well as 1,3-dibenzyl-THP (**3**) and its ring-opened product (**4**). ¹H NMR (500 MHz, 25°C, CDCl₃)

Several reaction conditions were tested to eliminate the double substitution of THP that occurred in the Finkelstein reaction. From these I found that the most important factor for reducing the double substitution is the molar ratio of the starting materials: Using at least four equivalents of THP (relative to VBC) resulted in high yields of the desired monosubstituted product. This was demonstrated by reaction 3l in **Table 2.3**, which may be considered my first successful synthesis of THPSt-HCl. In that synthesis, side products could be removed by column chromatography and the purified THPSt-HCl was confirmed by ^1H NMR spectroscopy, as shown in the black spectrum of **Figure 2.11**. The formation of THPSt-HCl is consistent with the presence of the methylene protons labelled **h** and **f**, which appear as two separate triplets due to the asymmetry of THPSt-HCl. This is in contrast to protons **h** and **f** of THP, which appear as a single triplet. Another notable transformation is that the methine proton singlet, **e**, has a strong downfield shift from 7.15 to 8.56 ppm due to the strong electron withdrawing character of the adjacent N-atom being positively charged as well as the styrene. Although the synthesis of THPSt-HCl was successful in the presence of excess THP, THPSt-HCl must be neutralized in order to capture CO_2 , as shown in Scheme 1.1. The neutralization procedure involves the use of NaOMe to deprotonate the amidine. The NMR spectrum of the protonated monomer (THPSt-HCl) and the resulting deprotonated monomer (THPSt) are shown in **Figure 2.12**. Two notable upfield shifts are observed for the methine proton (**d** to **d'**) and the methylene protons (**e** to **e'**, where **e'** is labelled in the zoomed-in inset spectral region). It is clear that the positive charge on the amidine group has a strong deshielding effect on adjacent protons, and that effect diminishes after deprotonation of the monomer to THPSt. Although we were able to synthesize the THPSt

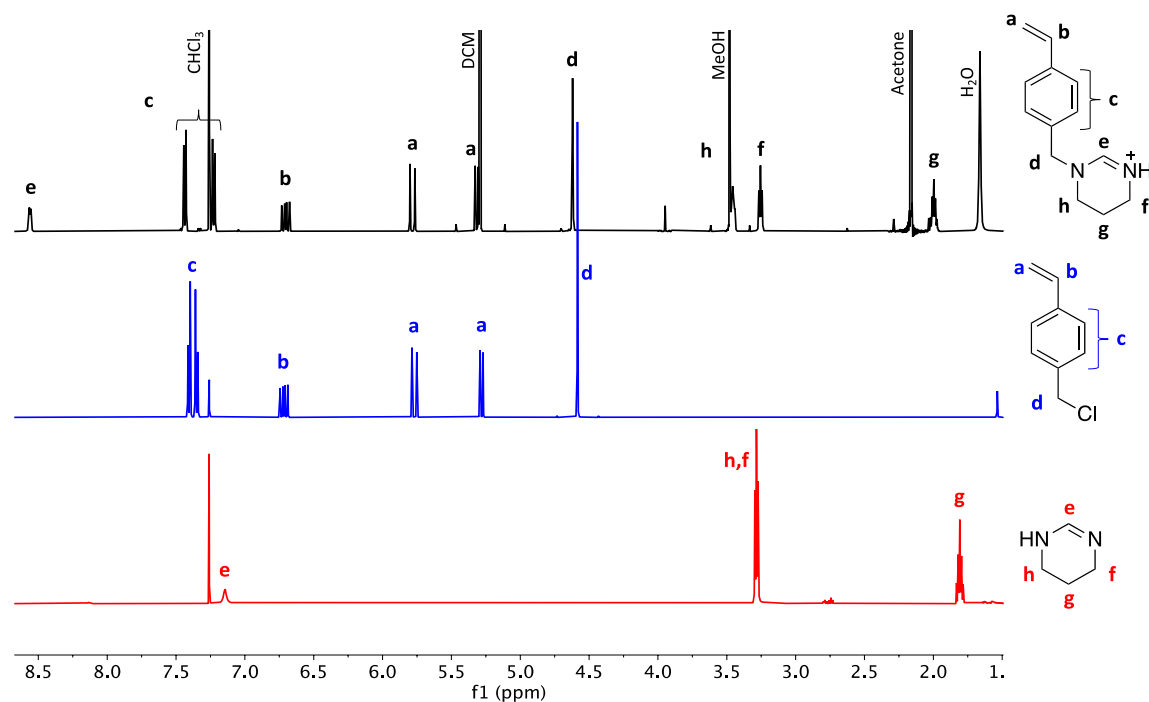


Figure 2.11. Stacked ^1H NMR spectra of the starting materials VBC (blue) and THP (red) and the isolated product, THPSt-HCl (black) resulting from a Finkelstein reaction using a molar ratio of VBC : THP of 4.2:1.0. ^1H NMR (500 MHz, 25°C , CDCl_3). Protons shifts for THPSt-HCl (top spectrum): δ , ppm: 2.44 (m, 2H, CH_2), 3.26 (t, 2H, CH_2), 3.46 (t, 2H, CH_2), 4.62 (s, 2H, CH_2), 5.30-5.34 (d, 1H, CH_2), 5.74-5.81 (d, 1H, CH_2), 6.66-6.74 (q, 1H, CH), 7.20-7.24 (d, 2H, arom. CH), 7.41-7.46 (d, 2H, arom. CH), 8.56 (d, 1H, CH).

monomer, it could not be polymerized by any free radical polymerization technique. Sakuragi et al. reported that the neutral THPSt could not be polymerized.⁶¹ Therefore, polymerization of the protonated monomer, THPSt-HCl, was attempted using an aqueous free radical polymerization. Unfortunately, using water as a solvent hinders our ability to synthesize copolymers due to the limited set of monomers amenable to free radical copolymerization in water. This presents an issue for developing copolymers with tailorable amidine content (by adjust the comonomer feed ratio) and adding other desired functionality (i.e., the addition of CO₂-philic groups). Therefore, a post-polymerization functionalized copolymers with controlled functionality.

2.6.3 Synthesis of THP-Functionalized Random Copolymers – Poly(St-*ran*-THPSt)

Post-polymerization modification of the copolymer, poly(St-*ran*-VBC), was used to obtain THP-functionalized copolymers. The degree of functionalization was controlled by adjusting the feed ratio in the random RAFT copolymerization of styrene and VBC monomers (Scheme 2.6), and then using Finkelstein reaction conditions to substitute THP at the benzylic chloride sites. Modification using the Finkelstein reaction was explored as a method to create THP (Scheme 2.7) to yield poly(St-*ran*-THPSt-HCl). The copolymers were then deprotonated by treatment with NaOMe to yield poly(St-*ran*-THPSt). These transformations were characterized by ¹H NMR spectroscopy and an example is shown in the stacked spectra presented in **Figure 2.13**. The starting copolymer, poly(St-*ran*-VBC), contained a molar ratio of St:VBC = 30:70 and is shown by the blue spectrum. It is worth noting that the blue spectrum was measured in CDCl₃, while the black, red, and green spectra were measured in methanol-d₄. This is due to the different solubility characteristics of the parent copolymer and the THP-functionalized copolymers. Despite this difference in the NMR solvents, the proton shifts for the THP-functionalized copolymers in

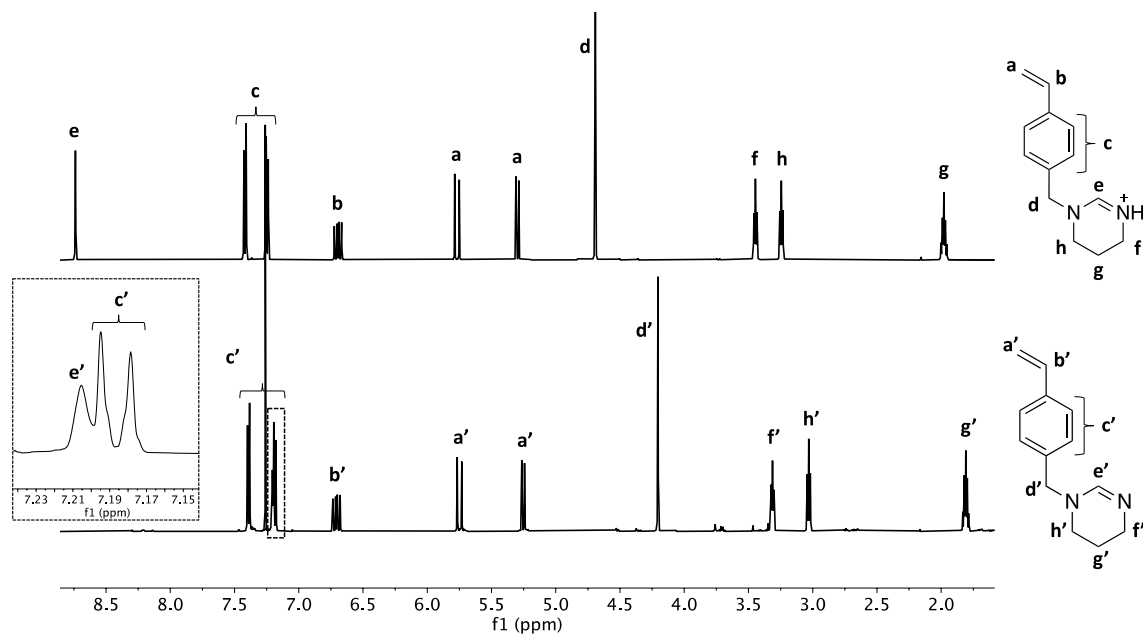


Figure 2.12. Stacked ^1H NMR spectra of THPSt-HCl and the isolated THPSt after deprotonation. ^1H NMR (500 MHz, 25°C , CDCl_3). THPSt proton shifts (bottom spectrum): δ , ppm: 1.81 (m, 2H, CH_2), 3.03 (t, 2H, CH_2), 3.31 (t, 2H, CH_2), 4.20 (s, 2H, CH_2), 5.23-5.27 (d, 1H, CH_2), 5.72-5.77 (d, 1H, CH_2), 6.66-6.74 (q, 1H, CH), 7.17-7.20 (d, 2H, arom. CH), 7.21 (d, 1H, CH), 7.37-7.41 (d, 2H, arom. CH).

methanol-d₄ can still be identified based on similar ¹H NMR spectra for THP-functionalized polymers reported by Sakuragi et al.⁶¹ The methine proton (**e**) is identified by the strong shift upfield from the black spectrum to the red spectrum as a result of deprotonation of the THP motifs on the copolymer. This behavior is consistent with deprotonation of THP-functionalized small molecule, THPSt-HCl, as shown in **Figure 2.12**. Additionally, an upfield shift of the **d** protons is observed as a result of deprotonation. shift is also consistent with the shifting behavior observed for deprotonation of the THPSt-HCl monomer (**Figure 2.12**). All the ring protons of THP (**e**, **f**, **g**, and **h**) are also shifted upfield due to the disappearance of the protonated amidine, which deshielded the surrounding protons. Finally, in order to identify the proton shifts associated with the ring-opened THP motifs (which are labelled **D**, **E**, **H**, **D'**, **H'** and **G'** in this spectrum), poly(*St-ran*-THPSt) was treated with KOH to induce ring-opening and opening occurs by attack of a hydroxide at the methine group and there are two possible the Resulting copolymer was analyzed by ¹H NMR as shown in the green sepectrum. Ring-opening mechanisms that yield either an aldehyde-terminated (repeat unit y₂) or an amine-terminated (repeat unit y₃) product, as reported by Sakuragi et al.⁶¹ For instance, the benzylic methylene protons of the amine-terminated product, **D'**, are shifted downfield due to the strong deshielding character of the adjacent aldehyde group, while the corresponding protons of the aldehyde-terminated product, **D**, are more upfield. Although the green spectrum (product of the KOH-induced ring-opening reaction) and previous reports by Sakuragi et al.⁶¹ helps identify the proton shifts associated with ring-opened THP motifs, the mixed functionality due to ring-opening of these copolymers makes it difficult to accurately calculate the copolymer composition. In addition, peaks such as **d** and **D'** in the black

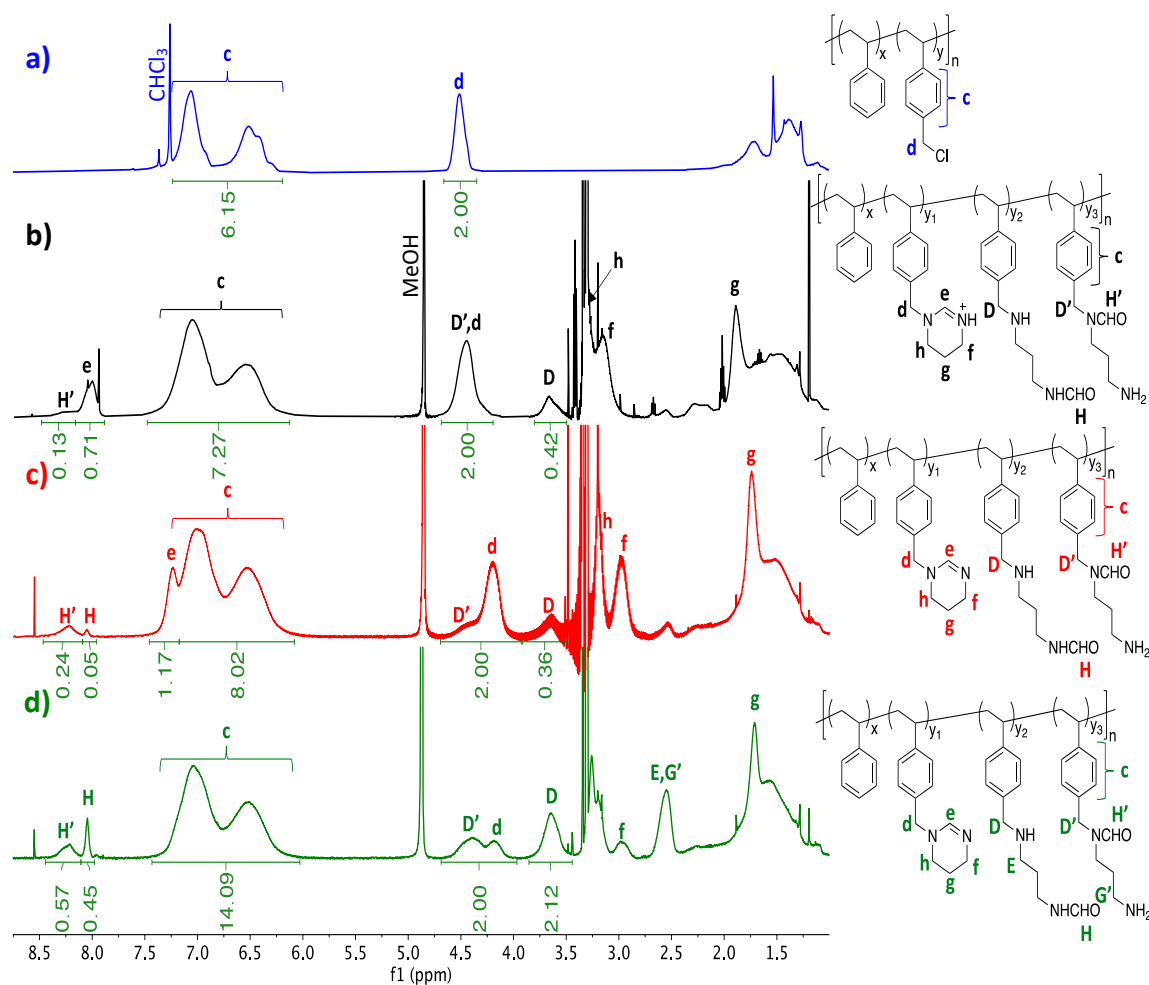


Figure 2.13. Stacked ^1H NMR spectra of a) poly(St-ran-VBC) as a result of RAFT copolymerization (blue spectra), b) (St-ran-THPSt-HCl) obtained from post-polymerization modification by the Finkelstein reaction (black spectra), c) poly(St-ran-THPSt) obtained from deprotonation by NaOMe (red spectra), and d) the ring-opened copolymer obtained from treatment with KOH (green spectra). a) ^1H NMR (300 MHz, 25°C , CDCl_3). b-d) ^1H NMR (500 MHz, 25°C , methanol- d_4).

spectrum overlap, making it impossible to calculate the composition based on those two protons. Furthermore, the ring-opening challenged the solubility of the copolymers. After precipitating and drying, all THP-functionalized copolymer samples were difficult to redissolve in common organic solvents. Partial solubility could be achieved if the polymer was quickly redissolved after precipitation, but after several days of storage at 4 °C, the copolymer only swelled by solvents – it could not be dissolved. This is most likely due to hydrogen bonding interactions that involved the amine and aldehyde groups, which led to crosslinking. Even adding a few drops of HCl to a solution of poly(St-*ran*-THPSt) in MeOH did not result in the copolymer becoming soluble. While it's possible that water-free reaction conditions and storage could reduce the potential for ring-opening reactions, Barkakaty et al.⁵⁷ and Endo et al.⁵⁰ both reported solubility issues with THP-functionalized copolymers that resulted in characterization issues and reduction of CO₂ adsorption capacity.

These results highlight the instability of THP during post-polymerization modification reactions, resulting in several issues including 1) loss of chemical uniformity and control over the composition (copolymer functionality), 2) reduction in CO₂ adsorption capacity, 3) difficulties in accurately characterizing the composition of the multi-component copolymer, and 4) insolubility driven by hydrogen bonding interactions. In addition, it is evident that the THP moiety presents several synthetic challenges, including 1) restriction to post-polymerization functionalization due to a tendency to participate in aza-Michael addition at any α,β -unsaturated carbonyl groups (which are prevalent in monomers for free radical polymerizations), 2) inability of THP-functionalized monomers to participate in free radical polymerizations, and 3) sensitivity to hydrolysis, ring-opening, and double substitution reactions. Due to these obstacles, it became prudent to explore

other amidine functional groups to continue our investigation on the physical and chemical behaviors of amidine-functionalized copolymers for CO₂ adsorption.

2.5 Conclusions

These studies provide a thorough understanding of issues of reactivity and behavior of the cyclic amidine, THP, in monomers and copolymers. Notably, THP prefers aza-Michael addition at the α,β -unsaturated carbonyl group of a vinyl monomer such as 2-HEA. The unwanted aza-Michael addition proceeds despite attempts to substitute THP at the terminal alcohol of 2-HEA by using 1) Mitsunobu Reaction conditions or 2) tosylation of the alcohol followed by nucleophilic substitution. Due to the competing aza-Michael addition reaction, the monomer of interest was changed to a styrene-based monomer, 4-vinylbenzyl chloride (VBC), which lacks the α,β -unsaturated carbonyl group. THP-functionalization of VBC was attempted by K₂CO₃- or KI-catalyzed substitution reactions. These efforts high stoichiometric excess of THP (THP : VBC = 4.2 : 1) results in successful substitution of THP at the halide site of VBC. Finally, THP-functionalization of poly(St-*ran*-VBC) copolymers was carried out by KI-catalyzed substitution reactions in a post-polymerization modification method. This synthetic route was required due to the inability to polymerize the neutral monomer, THPSt. However, the post-polymerization modification pathway suffered several disadvantages such as the complex functionality, instability, and insolubility of THP-functionalized copolymers made by post-polymerization modification. Although much information was garnered from our attempts to synthesize, polymerize, and characterize THP-functionalized monomers and copolymers, these routes made it impractical to develop THP-functionalized solid sorbent polymers for studies of CO₂ capture. In order to effectively study their physical and chemical responses of amidine-functionalized polymers in CO₂ capture, we abandoned THP-functionalized polymers and pursued a more stable

variant based on linear amidines, which, as detailed in Chapter 3 was amendable to efficient post-polymerization modification and enabled studies of CO₂ capture and release.

APPENDIX B

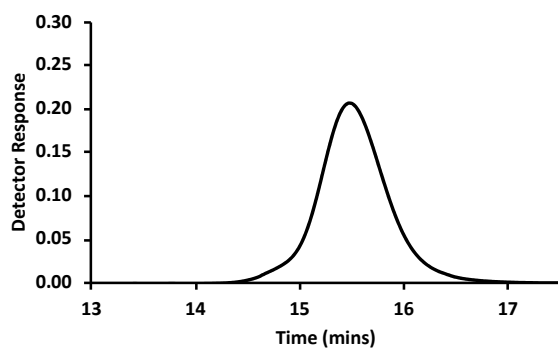


Figure B1. GPC trace of poly(St-*ran*-VBC) having 56 mol% VBC. This copolymer was synthesized by the procedure described in section 2.3.11. Based on conventional calibration, this copolymer had an $M_n = 10,800$ g/mol and a $\bar{D} = 1.11$.

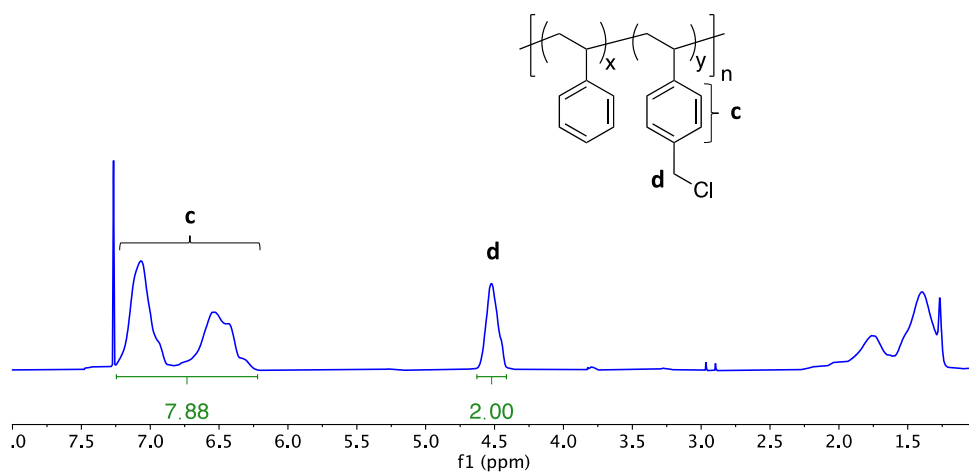


Figure B2. ^1H NMR spectrum for poly(St-*ran*-VBC) with a 56 mol% composition of VBC, as a result of the procedure described in section 2.3.11. ^1H NMR (500 MHz, 25°C, CDCl_3). δ , ppm: 1.22-2.28 (CH and CH_2 of polymer backbone), 4.51 (s, 2H, CH_3), 6.24-7.24 (arom. CH of styrenic ring).

CHAPTER III

**PHYSICAL AND CHEMICAL RESPONSES OF LINEAR AMIDINE-
FUNCTIONALIZED POLYMERS FOR THE CAPTURE AND RELEASE OF CARBON
DIOXIDE**

A version of this chapter will be submitted to *Macromolecules* and the authors are Danielle J. Chun, Abigail Mccord, Narges Mokhtari-Nori, Sheng Dai, Luke Daemen, Bradley S. Lokitz, and S. Michael Kilbey II.

S. Michael Kilbey was the corresponding author and was responsible for project oversight and contributed to writing of the article. All Neutron Vibrational Spectroscopy experiments and DFT calculations were completed by Luke Daemen. All other aspects of the project, including synthesis of functionalized copolymers and small molecules, execution of all characterization (TGA, optical microscopy, molecular characterization), and principal writing was completed by Danielle J. Chun.

3.1 Abstract

Polymeric materials containing amidine motifs are of high interest due to their ability to reversibly capture and release CO₂ at ambient temperature. Here we probe physical and chemical responses of styrene-based copolymers containing linear amidine motifs as functions of CO₂ and inert gas exposures and temperature. A copper-catalyzed azide-alkyne cycloaddition “click” reaction involving N'-propargyl-N,N-dimethylacetamidine is used to modify random copolymers, resulting in an array of linear amidine motifs along the chain backbone with the amount of CO₂-active amidine controlled by the copolymer composition. Through thermogravimetric measurements, we demonstrate that the amidine-functionalized copolymers efficiently capture CO₂ upon exposure to a stream of CO₂ (at 27 °C), and release it at a slightly elevated temperature (50 °C) when exposed to an inert gas stream (N₂). In addition to displaying a maximum adsorption capacity of 22 wt% in the presence of pure CO₂, the copolymers show composition-dependent direct air capture (DAC) behaviors. Small molecule analogs are used to definitively understand degradation via chemical hydrolysis of the amidine moiety, which leads to insolubility and a large reduction in CO₂ adsorption capacity (1.7 wt%). Neutron vibrational spectroscopy and DFT calculations confirm that CO₂ binds strongly to the amidine motif but a weak binding interaction also takes place at the triazole group. The coupled insights into mechanisms and behaviors of CO₂ adsorption in amidine-functionalized polymers provides a foundation for future investigations of CO₂-responsive polymers and soft materials to improve carbon capture and sequestration technologies.

3.2 Introduction

The cyclic amidine, 1,4,5,6-tetrahydropyrimidine (THP), has been widely explored for applications in CO₂ adsorption due to its high CO₂-fixing efficiency and reversible CO₂ capture/release properties. Unfortunately, as discussed in Chapter 2, the THP is sensitive to hydrolysis under mild conditions in the presence of adventitious amounts of water. This sensitivity to hydrolysis results in a loss of CO₂ adsorption capacity for the amidine-functionalized polymer systems, and also produces amide groups as a result of hydrolysis that increase network formation due to the increase in hydrogen bonding interactions.

Recent reports have noted the underappreciated hydrolytic instability of similar amidine compounds.^{103–106} For instance, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) is traditionally considered to be a sterically hindered and non-nucleophilic strong base. However, this description is only appropriate in relative terms: for instance, when carrying out reactions in organic solvent that require the deprotonating species to have a pK_a higher than amines. To develop a thorough understanding on the hydrolytic stability of various amidine compounds, Hyde et al. studied DBU, 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), and N,N,N',N'-tetramethylguanidine (TMG), where DBU and DBN are bicyclic amidines, MTBD and TBD are bicyclic guanidines, and TMG is a linear guanidine.¹⁰³ Each compound was dissolved in water at 27 °C and the degree of hydrolysis was measured for each after 4 h. As expected, the degree of hydrolysis for DBN, 32%, was much higher than that of DBU, 18%, due to the lower steric hindrance around the sp³-hybridized nitrogen for DBN. Also unsurprisingly, the guanidines showed a lower degree of hydrolysis (3.4% for MTBD and 3.8% for TBD) since guanidines are more stable than amidines due to their greater electron density at the sp²-hybridized carbon. However, Hyde and coworkers found that the linear

guanidine, TMG, hydrolyzed less than any other compound. This study reveals that linear guanidines are less susceptible to hydrolysis than their corresponding bicyclic guanidines, despite the lower steric hindrance around the linear guanidine, and suggests that linear amidines may be a more stable alternative for amidine-functionalized polymers.

Despite the small molecule studies by Endo et al. that claimed low CO₂ adsorption for linear-type amidines in solution,³⁴ linear amidines may offer a higher resistance to hydrolysis compared to THP as suggested by the work of Hyde et al.¹⁰³ In addition, polymers functionalized with linear amidines (as opposed to cyclic amidines such as THP) have demonstrated CO₂-fixing efficiency while possessing better solubility characteristics, enabling solution-state characterization and film casting from solution. For instance, Guo and coworkers used Cu-catalyzed azide-alkyne cycloaddition (CuAAC) “click” chemistry to functionalize poly(4-vinylbenzyl chloride) with linear amidine side groups.⁵⁹ The resulting CO₂-reponsive polymer was shown to exhibit a reversible hydrophobic-to-hydrophilic transition when alternately bubbling to CO₂ and N₂, respectively, through a CHCl₃/water biphasic solution. Similarly, Swager et al. synthesized an ethylene oxide-tethered styrene with a terminal azide, copolymerized this monomer with 4-vinylpyridine, and then modified the copolymer using CuAAC to install linear amidines in a manner analogous to Guo et al.⁵⁹ This copolymer was wrapped around single-walled carbon nanotubes and used for CO₂ sensing, demonstrating an experimental detection limit of 0.2% CO₂ from a mixed-gas stream of CO₂ and N₂.⁶⁰

Amidine-functionalized polymers offer compelling potential in sensing or capture applications, but the impact of environmental factors (e.g. heat and moisture content in the gas stream) on the physical or chemical changes is yet to be fully elucidated, potentially because of the aforementioned solubility issues in Chapters 1 and 2. To address this, we study a series of

styrene-based copolymers that contain linear amidine motifs, which are synthesized based on procedures reported by Guo et al.⁵⁹ The amidine-functionalized homopolymer, poly(VBTAm), achieved high CO₂ adsorption when challenged by pure CO₂ (comparable among the top performing porous organic polymers)⁶² that can be reversed when exposed to the inert gas N₂ with gentle heating. The ability of the linear amidine-containing copolymers to capture CO₂ at atmospheric concentrations is examined using a series of compositionally-controlled copolymers. We also confirm that the amidine motifs on the copolymers are principally responsible for CO₂-fixing, as revealed by neutron vibrational spectroscopy (NVS) combined with density functional theory (DFT) calculations. Finally, we elucidate the chemical outcome of hydrolysis, which gives rise to hydrogen bonding interactions that lead to insolubility and network formation. This comprehensive analysis of capture/release behaviors, thermal properties, and hydrolysis behavior provides unparalleled insights into the physical and chemical responses of amidine-containing polymers for CO₂ adsorption.

3.3 Experimental

3.3.1 Materials

All reagents were used as received unless stated otherwise. 2,2'-Azobis(2-methylpropionitrile) (AIBN) was purchased from Sigma-Aldrich and recrystallized from methanol to obtain needle-like crystals before use. All small molecules, including benzyl chloride, 4-vinylbenzyl chloride and styrene were purchased from Fisher Scientific. All monomers were passed through a basic alumina column to remove inhibitors. Dry N,N-dimethylformamide (DMF) was obtained from an Innovative Technologies PureSolv Solvent Purification System. Acetonitrile was purchased from Fisher Scientific and used as received. Copper(I) bromide was obtained by stirring copper(II) bromide (Sigma Aldrich) in excess glacial

acetic overnight, followed by recovery and purification by filtration and washing with methanol and anhydrous diethyl ether. Cylinders of CO₂ (Pure Clean, 99.995% purity) for thermogravimetric analysis (TGA) were purchased from Airgas and used as received. Cylinders of CO₂ (400 ppm CO₂, 400 ppm argon, balanced in helium) and cylinders of helium (Ultra High Purity Grade) for direct air capture (DAC) experiments were purchased from Airgas and used as received.

3.3.2 Instrumentation and Characterization.

3.3.2.1 NMR Spectroscopy.

¹H, ¹³C, and ¹³C (APT) NMR spectra were collected on a Varian VNMRS 500 MHz NMR at room temperature in chloroform-*d* (CDCl₃). The residual solvent peak served as an internal standard.

3.3.2.2 Gel Permeation Chromatography (GPC).

Number-average molecular weight (M_n) and dispersity ($\mathcal{D}$) were determined using an Agilent 1260 Infinity II GPC system using THF at a flow rate of 1.0 mL/min as the mobile phase. The system was equipped with a Wyatt Dawn Helios 8 multiangle light scattering detector and Viscostar III and Optilab T-rEX detectors. Values of M_n and $\mathcal{D}$ are reported based on conventional calibration analysis using polystyrene standards. Samples were prepared in HPLC-grade THF at a concentration of 5 mg/mL and filtered through a 2.0 μ m PTFE filter prior to injection.

3.3.2.3 Thermogravimetric Analysis (TGA).

Degradation temperatures (T_d) were measured using a TA Instruments Q50 TGA. The temperature was ramped from 25 to 600 °C at a rate of 10 °C/min under a nitrogen atmosphere.

Gas adsorption and desorption studies of the amidine-functionalized copolymers utilized a TA Instruments Discovery Series TGA. In a typical experiment, ~10 mg of copolymer was added to a platinum pan and loaded into the TGA instrument. The sample was initially preconditioned by

heating to 50 °C under a pure, dry N₂ atmosphere at a flow rate of 20 mL/min and the temperature maintained for 60 minutes to release any adsorbed moisture or CO₂. After this protocol, the temperature was equilibrated to 27 °C under N₂ flow.

To examine CO₂ capture and release behaviors, the preconditioned sample was exposed to pure CO₂ at 27 °C for 120 minutes at a flow rate of 20 mL/min. After CO₂ exposure, the gas was switched to pure N₂ at a flow rate 20 mL/min and the temperature was ramped to 50 °C. The temperature was held isothermally for 60 minutes while monitoring CO₂ release. Each sample was subjected to at least 3 adsorption/desorption cycles to investigate repeatability.

3.3.2.4 Differential Scanning Calorimetry (DSC).

The glass transition temperature (T_g) of each copolymer was measured using a TA Instruments Q2000 DSC. In a typical procedure, 2-4 mg of the copolymer was added to an aluminum pan that was sealed by crimping and then subjected to a heat/cool/heat cycle between 25 to 185 °C at a rate of 10 °C/min. The TA Universal Analysis program was used to determine the T_g from the midpoint of the transition observed on the second heating cycle.

3.3.2.5 Direct Analysis in Real Time (DART) Mass Spectrometry.

High-resolution masses of small molecule products were measured by time-of-flight direct analysis in real time mass spectrometry (DART-MS) using a JEOL AccuTOF DART mass spectrometer. Samples were prepared at concentrations between 20 µg/mL and 1 mg/mL using toluene as the solvent. The standard peak voltage was between 600-800 V and the detector voltage was set to 2300 V.

3.3.2.6 Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR).

ATR-FTIR spectra were obtained using a Bruker Alpha II spectrometer with a diamond ATR crystal for ATR measurements. All samples were deposited directly onto the diamond crystal for

analysis. Polymer samples were measured as dry solids using the platinum anvil. Small molecules were dissolved in toluene and deposited directly onto the ATR crystal without the use of the anvil. The instrument resolution was 4 cm^{-1} and each spectrum was generated using 64 scans.

3.3.2.7 Direct Air Capture of CO₂ using a Non-dispersive Infrared (NDIR) CO₂/H₂O Gas Analyzer.

A custom-built direct air capture system was used to measure CO₂ capture capacity as described previously by Moitra et al.¹⁰⁷ The NDIR gas analyzer (LI-850/LI-COR) continuously monitors the concentration of both CO₂ and water in the outlet stream. Prior to each experiment, the system is purged of water by using dry helium at a flow rate of 90 mL/min at ambient temperature. Following this, the infrared detector is calibrated for dry conditions. The gas is then switched to CO₂ (400 ppm CO₂, 400 ppm argon, balanced in helium) at a flow rate of 40 mL/min to calibrate the detector to 400 ppm of CO₂. After both calibrations, the sample is added to a glass column reactor where the copolymer sample (~ 16 mg) was positioned between two pieces of fibrous glass wool. Then, atmospheric gases and water are desorbed from the sample by passing dry helium at flow rate of 90 mL/min through the sample at 50 °C until the detector achieves a stable baseline consistent with 0 ppm of CO₂. After this, the reactor temperature is equilibrated to 25 °C, data collection is started, and the gas is quickly switched to CO₂ (at 400 ppm) at a flow rate of 40 mL/min. CO₂ capture was monitored until the detector achieved a stable reading consistent with 400 ppm of CO₂. At this time, data collection is stopped.

3.3.2.8 Optical Microscopy.

A Leica M165-C Stereomicroscope installed with a Flexacam C3 12 MP Microscope Camera was used to image particle sizes of amidine-functionalized copolymers. A small amount of polymer powder was placed on a glass slide and then covered with a cover slip. The polymer was

ground to fine particles by applying friction between the glass slide and the cover slip and then analyzed under the microscope.

3.3.2.9 *Inelastic Neutron Scattering (INS).*

Neutron vibrational spectroscopy was performed using the VISION spectrometer at the Spallation Neutron Source at Oak Ridge National Laboratory. A 100 mg copolymer sample was loaded into a 6 mm vanadium sample holder and exposed to a flow of dry N₂ at 50 °C for 2 h to desorb any bound gases. The sample was then cooled to 5 K in the closed-cycle refrigerator at the VISION beam line and a spectrum was acquired to be used as a background. The sample was then exposed to 1 bar of CO₂ and was allowed to equilibrate for approximately 2 h at 50 °C. After this time, the cell temperature was held at 27 °C for 1 h. A neutron vibrational spectrum for the CO₂-adsorbed sample was then acquired at 5K. The data sets were reduced with the MantidWorkbench software. The data reduction consisted mainly in rebinning the histograms and applying smoothing (moving average) to remove the noise in the difference spectrum between the CO₂-loaded spectrum and the reference spectrum (no CO₂).

3.3.3 **Synthesis of Random Copolymers.**

3.3.3.1 *Synthesis of Parent Copolymer - Poly(St-*ran*-VBC).*

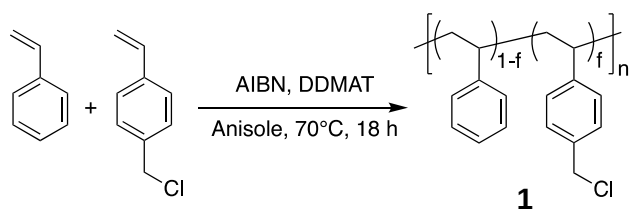
Random copolymers were synthesized via reverse addition-fragmentation chain transfer (RAFT) polymerization as shown in Scheme 3.1. As an example, an equimolar feed ratio of comonomers was used for the preparation of **1f₅₆**, where **f₅₆** identifies the resulting composition (56 mol%) of VBC in poly(St-*ran*-VBC). Styrene (2.32 g, 22.3 mmol) and VBC (3.40 g, 22.3 mmol) were added to a 5 mL round bottom flask containing AIBN (7.61 mg, 0.0463 mmol) and 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT) (84.5 mg, 0.232 mmol) that was pre-dissolved in dry anisole (4.3 mL). A magnetic stir bar

was added, and the flask sealed with a rubber septum. The contents were sparged with argon for 20 min and then the flask was lowered into an oil bath preheated to 70 °C. After 18 h, the reaction was quenched by removing the septum and immersing the flask in liquid nitrogen until the contents completely froze. After thawing, the solution was diluted with THF and then precipitated into a large excess of hexanes. The solids were collected by gravity filtration and then redissolved in THF. This cycle was repeated twice more to yield a fluffy yellow powder. The solid copolymer was dried at 30 °C overnight under vacuum. The number-average molecular weight determined by GPC relative to polystyrene standards was $M_n = 10,800$ g/mol and the dispersity $\bar{D} = 1.11$. Molar composition was determined via ^1H NMR to be 56 mol% VBC as assessed from the benzylic methylene at 4.51 ppm and aromatic protons that appear in the range from 6.20-7.24 ppm (See **Figure C1.**) as noted in the Article. Other copolymer compositions were obtained by adjusting the comonomer feed ratio, and the results are shown in **Table 1**.

3.3.3.2 *Synthesis of Azide-Functionalized Copolymer – Poly(St-ran-VBTaz).*

The azide copolymer derivative, **2f₅₆**, was synthesized according to procedures reported by Guo et al as shown in Scheme 3.2.⁵⁹ As an example, copolymer **1f₅₆** (2.80 g, 11.6 mmol of VBC repeat units) was added to a flame-dried 100 mL round bottom flask containing dry DMF (35.0 mL) and a stir bar. Sodium azide (3.77 g, 58.0 mmol) was then added to the dissolved polymer

Scheme 3.1. RAFT copolymerization of styrene and 4-vinylbenzyl chloride to yield poly(*St-ran-VBC*) (**1**).

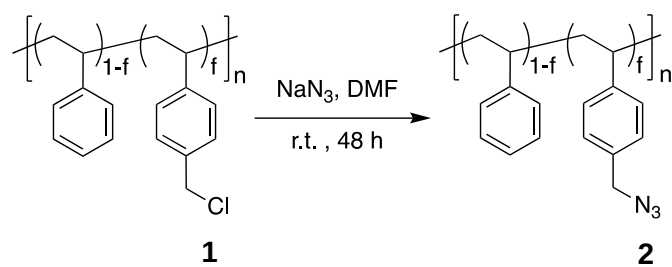


solution. The reaction was sparged with argon for 20 minutes and then allowed to stir at room temperature for 48 h. After this time, the reaction mixture was precipitated into methanol and collected by gravity filtration as a white fluffy powder. The isolated copolymer was dried in a vacuum oven overnight at room temperature to yield copolymer **2f**₅₆. The yield was determined to be 87% by mass. As shown in **Figure C3**, the composition was determined by ¹H NMR using resonances associated with the methylene of the benzyl azide (4.51 ppm) and the aromatic protons (6.23-7.23 ppm). The absence of protons associated with the methylene of benzyl chloride (δ = 4.51 ppm, as seen in **Figure C1**) indicate complete conversion.

3.3.3.3 *Synthesis of Amidine-Functionalized Copolymers - Poly(St-ran-VBTAm).*

Copolymers were synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization. The copolymer composition was controlled by adjusting the feed ratio of styrene (St) and 4-vinylbenzyl chloride (VBC) to yield random copolymers of poly(St-ran-VBC) (which are identified as **1** in Scheme S1 in the Supporting Information). Copolymer composition is represented by the subscripted number attached to “f”, which is the mole percent of VBC in the copolymer. Monomer feed ratios and the resulting copolymer compositions, M_n , and Đ are given in **Table 1**. Complete details on the procedures, reaction conditions, and characterization for poly(St-ran-VBC) are reported in the Supporting Information. To install amidine groups, the poly(St-ran-VBC) was first reacted with sodium azide salt to yield poly(St-ran-VBAz) (**2**), and then “clicked” with N'-propargyl-N,N- dimethylacetamide (PDAA) by Cu-catalyzed azide-alkyne cycloaddition (CuAAC) to yield the amidine-functionalized copolymer, poly(St-ran-(4-vinylbenzyl)-1,2,3-triazol-4-dimethylacetamide), which we refer to throughout this Article as poly(St-ran-VBTAm) (**3**).⁵⁹ This synthetic approach, which is depicted in Scheme 1, follows the approach described by Guo et al.⁵⁹

Scheme 3.2. Sodium azide S_N2 substitution to yield poly(St-*ran*-VBaz) (**2**).



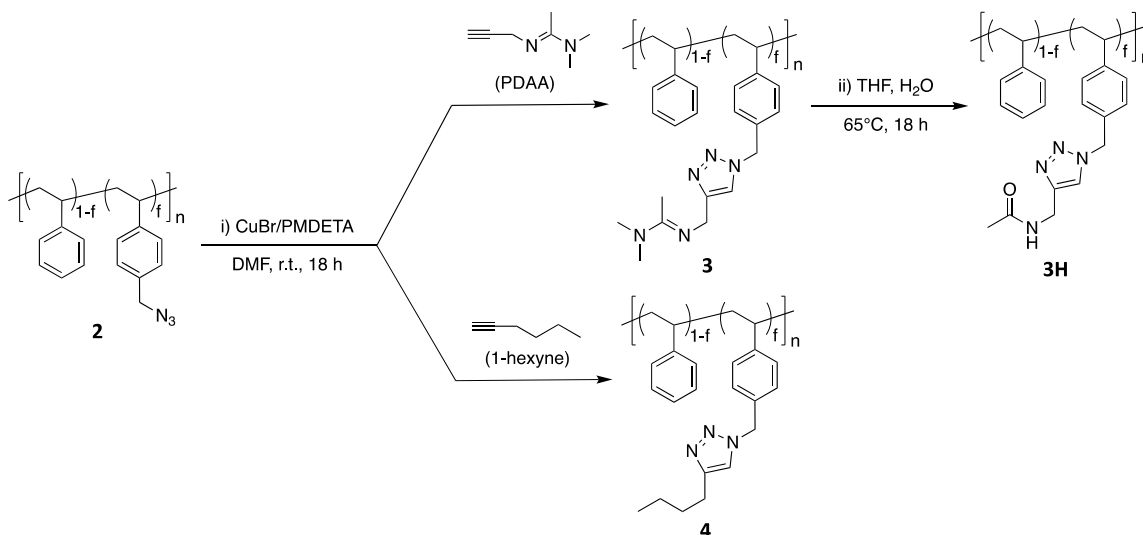
As an example, the procedure for amidine-functionalization of **2f₁₀₀** (**f₁₀₀** designates the amidine composition) by CuAAC “click” chemistry is described here. Copper (I) bromide (43.3 mg, 0.302 mmol) was combined with N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDTA) (52.3 mg, 0.302 mmol) in a flame-dried 100 mL round bottom flask. A mixture of **2f₁₀₀** (0.300 g, 1.88 mmol of azide-containing repeat units), PDAA (0.632 g, 5.08 mmol), and dry DMF (5.5 mL) was then added to the reaction flask. Three freeze-pump-thaw cycles were used to remove dissolved oxygen. The reaction flask was backfilled with argon and the mixture stirred at room temperature for 18 h. After this time, the crude product mixture was passed through a basic alumina plug to remove copper bromide. DMF was removed by precipitating the crude product solution into diethyl ether and decanting the solvent. The precipitate was redissolved in CHCl₃ to create a dilute solution, which was then precipitated into hexanes. The solids were isolated by decanting (Note: gravity filtration was not used because the copolymer strongly absorbed to the filter paper.)

This process of isolating the solid, redissolving to create a dilute solution, and precipitating in hexanes was performed a total of 3 times. The purified, isolated solids were obtained as a reddish-brown fluffy powder that was dried under vacuum at room temperature and stored under argon at 4 °C. ¹H NMR and ATR-FTIR spectroscopies were used to confirm conversion from the azide-functionalized starting material (**2**) to the amidine-functionalized form (**3**), and these spectra are reported in the Supporting Information.

3.3.3.4 *Synthesis of Hydrolyzed Polymers - Poly(St-ran-VBTAmH) (**3H**).*

Procedures from Hollockzi et al. to hydrolyze small molecule imidazoles⁹⁸ are adapted to enable hydrolysis of amidine-functionalized copolymers. In a typical experiment, copolymer **3** (0.200 g) was dissolved in tetrahydrofuran (2 mL). Approximately 2 drops of water were added and the solution refluxed at 65 °C overnight. Then, the solution was precipitated into ethyl acetate.

Scheme 3.3. Strategy for synthesizing poly(*St-ran*-VBTAm) (3). (i) Cu-catalyzed azide-alkyne cycloaddition (CuAAC) between azide side groups and PDAA yields the amidine-functionalized copolymer (3) or the alkylated copolymer (4). (ii) Hydrolysis of the amidine groups on 3 yields the hydrolyzed copolymer (3H) bearing amide groups.



It was found that all of the hydrolyzed copolymers except **3Hf₁₃** became completely insoluble, making them impossible to characterize by NMR spectroscopy. However, the hydrolyzed copolymer, **3Hf₁₃**, was soluble in deuterated chloroform, and the progression of hydrolysis was examined by withdrawing aliquots and analyzing each by ¹H NMR spectroscopy, as shown in **Figure C6**.

3.3.3.5 *Synthesis of Alkylated Copolymer - Poly(St-ran-VBTB) (4).*

An alkylated copolymer bereft of amidine functionality was synthesized following the same procedures described for poly(St-ran-VBTAm), as shown in Scheme 1. However, instead of PDAA, 1-hexyne was used to generate poly(St-ran-(4-butyl-1-(4-vinylbenzyl)-1*H*-1,2,3-triazole)), which we refer to as poly(St-ran-VBTB) (**4**). Only a single copolymer was alkylated, **4f₅₆**, and this copolymer was characterized by ¹H NMR spectroscopy, as shown in **Figure C7**, and by ATR-FTIR spectroscopy, as described later.

3.3.4 Synthesis of Small Molecules.

3.3.4.1 *N'-Propargyl-N,N-dimethylacetamidine (PDAA).*

The small molecule amidine “click” reagent, PDAA, was synthesized following a procedure reported by Swager et al. (Scheme S3).⁶⁰ PDAA was recovered in quantitative yields and stored under argon at 4 °C. ¹H NMR spectroscopy confirmed the structure (**Figure C8**).

3.3.4.2 *Synthesis of Benzyl Azide.*

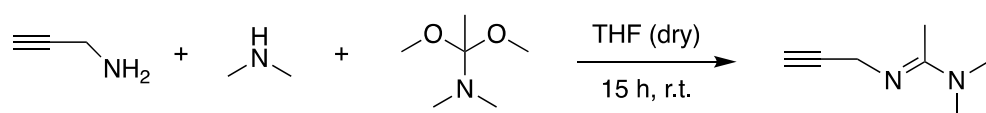
Benzyl azide was synthesized from benzyl chloride as shown in Scheme 3.4. In brief, benzyl chloride (1.00 g, 7.9 mmol) was dissolved in a mixture of anhydrous DMF (3 mL) and acetonitrile (ACN) (50 mL). Sodium azide (0.767 g, 11.8 mmol) was added to the reaction mixture and the mixture refluxed for 24 h while stirring. The crude product was diluted with deionized water (50 mL) and extracted with dichloromethane (3 × 30 mL). The combined organic layers were then

washed with deionized water (3×30 mL). The collected organic layer was dried over magnesium sulfate (MgSO_4) and solvent was removed by rotary evaporation at reduced pressure. The product, recovered as a clear oil, was analyzed by ^1H NMR spectroscopy. ^1H NMR (500 MHz, 25°C , CDCl_3). δ , ppm: 4.34 (s, 2H, CH_2), 7.30-7.41 (arom. CH of styrenic ring). Benzyl azide serves as the starting material for the preparation of amidine-containing small molecule analogs of the copolymers.

3.3.4.3 Synthesis of ((1-benzyl-1,2,3-triazole-4-yl)methyl)-N,N-dimethylacetamide.

The small molecule analog of the amidine-functionalized repeat unit of copolymer **3**, will be referred to as “benzyl-TA”, and was prepared by a procedure similar to the “click” reaction used to create amidine-functionalized copolymers. Briefly, CuBr (54.2 mg, 0.378 mmol), PMDTA (65.5 mg, 0.378 mmol), benzyl azide (0.689 g, 2.36 mmol) and dry DMF (12.6 mL) were added to a round bottom flask containing a stir bar. PDAA (0.425 g, 3.19 mmol) was added dropwise. Following this addition, the flask was capped with a rubber septum and subjected to three freeze-pump-thaw cycles. After evacuation on the third cycle, the flask was back-filled with argon and then allowed to thaw. The mixture was stirred at room temperature for 18 h. After this time, 15 mL of CHCl_3 were added and the reaction mixture, which then was extracted with DI water ($50 \text{ mL} \times 3$). The organic phases were collected and dried over MgSO_4 . The MgSO_4 was removed by gravity filtration and the filtrate was evaporated under reduced pressure to yield “benzyl-TA” as a dark red liquid. ^1H and ^{13}C APT NMR techniques, **Figure 8** and **Figure C10**, were used to confirm the structure of “benzyl-TA”. The mass determined by high-resolution mass spectrometry (HRMS) using DART-MS is presented in **Figure C11a**.

Scheme 3.4. Synthesis of N'-propargyl-N,N-dimethylacetamidine (PDAA).



3.3.4.4 *Synthesis of ((1-benzyl-1,2,3-triazol-4-yl)methyl)acetamide.*

The small molecule analog to the hydrolyzed repeat unit of copolymer **3H**, which will be referred to as “benzyl-TAH”, was prepared by exposing “benzyl-TA” for three days to a constant flow of moist air that was created by bubbling air through deionized water. The crude oil was analyzed by high-resolution mass spectroscopy (HRMS) using DART-MS, and the result is presented in **Figure C11b**. The hydrolyzed product was isolated by passing the resulting oil through a neutral alumina column using DCM and 5% MeOH as the eluent. The final product was recovered as a light brown oil. ^1H and ^{13}C APT NMR techniques were used to confirm the structure of “benzyl-TAH”, and these are presented in **Figure 8** and **Figure C10**, respectively.

3.4 Results and Discussion

3.4.1 Amidine-Functionalized Random Copolymers.

3.4.1.1 *Synthesis and Characterization of Amidine-Functionalized Copolymers (3).*

Copolymers of styrene and 4-vinylbenzyl chloride (VBC) at four different molar compositions were synthesized by RAFT polymerization following procedures similar to those reported by Guo et al.,⁵⁹ which are summarized in the Supporting Information and shown in Scheme S1. This strategy resulted in polymers of narrow dispersity ($\text{Đ} = 1.11\text{--}1.15$) and similar molecular weights ($M_n \approx 12$ kDa) as shown in **Table 3.1**. These copolymers, poly(St-*ran*-VBC), are denoted generally as **1** and their molar composition of VBC is represented by the subscript on **f**: for example, **1f₅₆** represents a poly(St-*ran*-VBC) copolymer with 56 mol% VBC functionality. Copolymers of type **1** serve as parent copolymers that are reactively modified to create amidine-containing copolymers. Reactions of **1** with sodium azide, which are also described in the Supporting Information (as shown in Scheme S2), resulted in complete conversion to the azide form, as evidenced from the ^1H NMR spectra presented in **Figure 3.1**. We refer to this set of

Table 3.1. Macromolecular characteristics of poly(St-*ran*-VBC) (**1**) copolymers.

Polymer Name	Comonomer Feed Ratio (St : VBC)	Copolymer Composition (1-f) : f	M_n (kg/mol)	$\bar{D}$
1f₁₀₀	0 : 100	0 : 100	13.1	1.14
1f₅₆	50 : 50	44 : 56	14.1	1.11
1f₃₀	75 : 25	70 : 30	11.0	1.14
1f₁₃	90 : 10	87 : 13	10.2	1.15

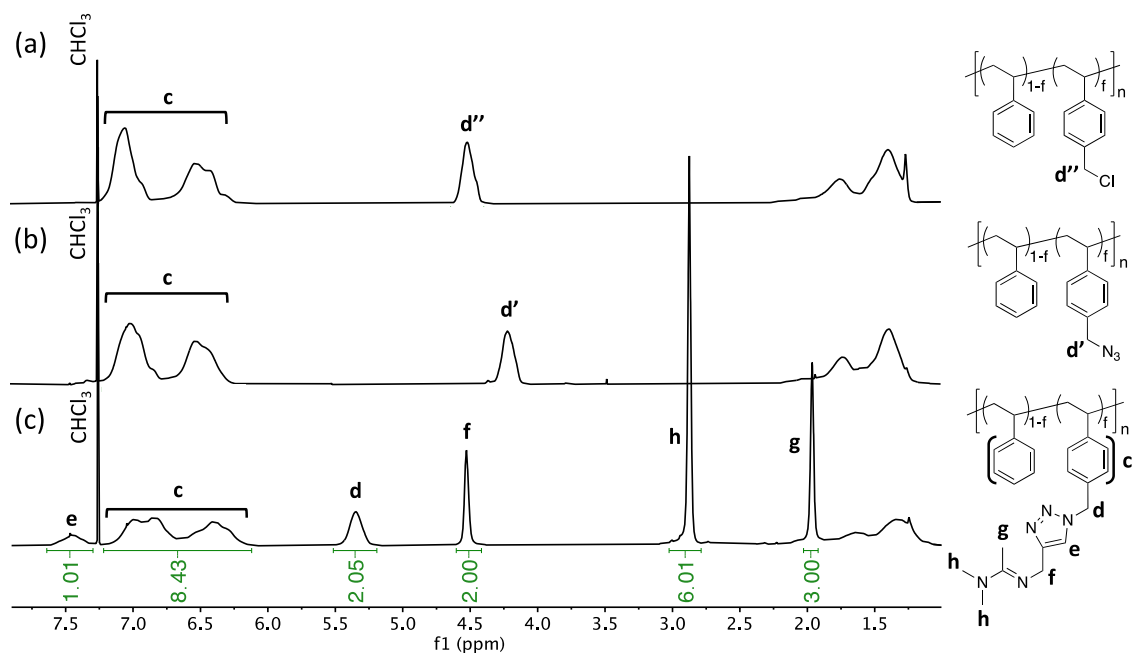


Figure 3.1. Stacked ^1H NMR spectra of (a) poly(St-*ran*-VBC) (**1f₅₆**) (b) poly(St-*ran*-VBAz) (**2f₅₆**) and (c) poly(St-*ran*-VBTAm) (**3f₅₆**).

alkyne copolymers as poly(St-*ran*-VBaz) (**2**). The linear amidine motif was installed by Cu-catalyzed azide -cycloaddition (CuAAC), where N'-propargyl-N,N-dimethylacetamide (PDAA) was “clicked” onto the azide-functionalized copolymer. For convenience, we refer to these copolymers as poly(St-*ran*-VBTAm) (**3**) and present in **Figure 3.1a** the ^1H NMR spectrum that confirms the successful synthesis of **3f₅₆** (along with spectra from the parent copolymers **1f₅₆** and **2f₅₆**). Additional details obtained from ^1H NMR spectroscopy of all copolymers of **1**, **2**, and **3** are reported in the Supporting Information in **Figures C1**, **C3**, and **C4**, respectively. ATR-FTIR spectroscopy also confirms success of CuAAC reaction. As shown in **Figure C5**, the azide stretch that is clearly observed at 2103 cm^{-1} for poly(St-*ran*-VBaz), is not seen in the spectrum for the corresponding poly(St-*ran*-VBTAm).

3.4.1.2 *CO₂ Adsorption Behaviors of Amidine-Functionalized Copolymers.*

Thermal gravimetry was used to study the ability of the amidine-functionalized homopolymer, **3f₁₀₀**, to capture CO₂ using a flow of pure CO₂. The sample was subjected to multiple cycles of CO₂ flow (at 27 °C) followed by N₂ flow (at 50 °C) to assess reversible capture and release behaviors. For **3f₁₀₀**, a CO₂ adsorption capacity of 22 wt% was achieved and the process was reversible over three cycles, as reported in **Figure 3.2a**. The highest CO₂ adsorption capacity for amidine-functionalized linear polymers was reported by Endo et al. for their styrenic polymer that contained the monocyclic amidine motif, THP. A capture efficiency of 73 mol% CO₂/amidine was reported when the polymer was dissolved in DMF and exposed to CO₂ by bubbling. However, when tested as a dry solid sorbent, its CO₂ capture efficiency dropped to 12 mol% CO₂/amidine.⁵⁰ This result is comparable to the fixing efficiency reported by Barkakaty et al. for THP-modified PVDMA-based polymer, which adsorbs 10-11 mol% CO₂/amidine (reported as 0.34 mmol CO₂/g polymer).⁵⁷ By comparison, our linear amidine

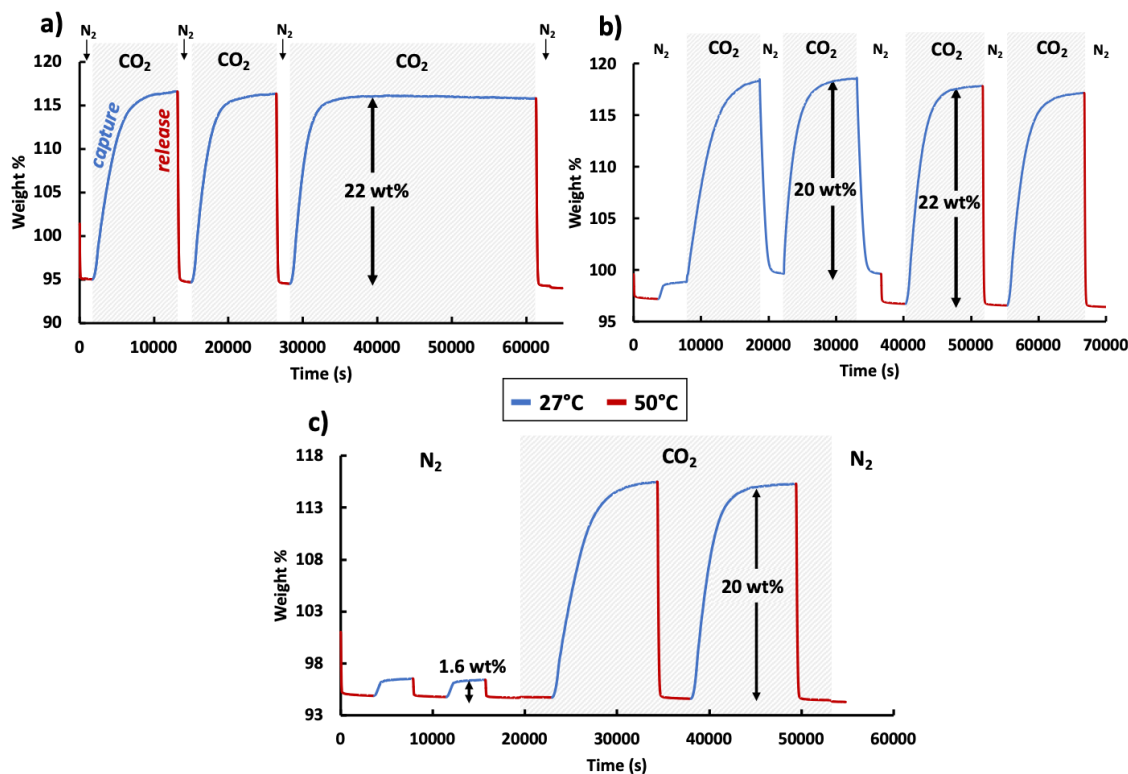


Figure 3.2. TGA profiles reflecting the capture and release behaviors of $3f_{100}$. The chamber temperature is controlled at either at 27 °C (blue lines) or 50 °C (red lines) while being exposed to a flow of either N_2 gas (unshaded regions) or pure CO_2 gas (shaded regions). Experiments were implemented to analyze the behavior of gas adsorption and release under various conditions: (a) A typical procedure is shown for reversible CO_2 capture and release over three cycles. (b) CO_2 release is demonstrated at both 27 °C and 50 °C. (c) The adsorption capacity of N_2 (1.6 wt%) and CO_2 (20 wt%) are demonstrated separately.

functionalized homopolymer, **3f₁₀₀**, captures CO₂ at 5.28 mmol CO₂/g polymer, as a solid sorbent. As shown in **Table 2**, the value measured for **3f₁₀₀** is of the same order of magnitude as the values observed for porous organic polymers (POPs).^{62–67}

In addition, we probed the efficacy of CO₂ desorption at 27 °C and at 50 °C, and the results are shown in **Figure 3.2b**. This experiment began with an N₂ purge at 50 °C followed by equilibration at 27 °C while continuing the N₂ flow. After thermal equilibration, the flow was switched to CO₂ gas and mass uptake was monitored until a stable mass was achieved. At this point, CO₂ desorption was triggered by changing the gas flow to N₂ at 27 °C (first two cycles) or to N₂ at 50 °C (last two cycles). While both desorption protocols demonstrate release of CO₂, desorption with N₂ flow at 27 °C leaves a small adsorbed mass (~2 wt%) that is only desorbed when the temperature is ramped to 50 °C under N₂ flow. This small adsorbed mass unmistakably corresponds to N₂ gas, as demonstrated in **Figure 3.2c**: the first two adsorption peaks clearly indicate N₂ uptake by **3f₁₀₀** when subjected to pure N₂ flow at 27 °C with a return to baseline at 50 °C.

For comparison, we also studied CO₂ desorption using only a temperature swing while maintaining CO₂ flow using polymer **3f₁₀₀**, as shown by the last two capture/release cycles in **Figure 3.2c**. It is clear from the experiment that the amidine group has a strong preference for binding CO₂ (rather than N₂) at 27 °C, and raising the temperature to 50 °C results in release of CO₂ to the same level achieved under N₂ at 50 °C, as shown by the continuity of the baseline when the flow is switched from N₂ to CO₂ at 50 °C (intersection of shaded/unshaded areas at 20,000 s and 52,500 s). These results highlight important preferences in the adsorption behavior and demonstrate complete reversibility of capture/release by mild heating. In total, these sets of experiments demonstrate that the amidine-functionalized polymer effectively captures CO₂ when

exposed to pure CO₂. Therefore, it is also relevant to assess the ability of these linear amidine-containing copolymers to capture CO₂ at atmospheric concentrations.

3.4.1.3 Direct Air Capture.

Direct air capture (DAC) experiments were used to demonstrate the ability of amidine-functionalized copolymers of various composition (**3f₁₃**, **3f₃₀**, **3f₅₆**, and **3f₁₀₀**) to capture CO₂ at atmospheric concentrations (400 ppm). A nondispersive-infrared (NDIR) gas analyzer was used to monitor CO₂ adsorption, and an example of the output generated is shown in **Figure 3.3a** for **3f₁₀₀**. These data are recast in the form shown in **Figure 3.3b**, and the area under the curve (6.641 mins) is used in Eqn. 1 to calculate the amount of CO₂ adsorbed on a per mass of polymer basis, as reported in **Table 3**. The CO₂ adsorption capacity for **3f₁₀₀** under DAC conditions (0.287 mmol CO₂/g polymer) is much lower than that measured by TGA (5.28 mmol CO₂/g polymer) when the polymer was exposed to a flow of pure CO₂. However, despite the low CO₂ concentration used in the DAC experiments, the adsorption capacity under DAC conditions is comparable to that reported by Barkakaty et al. for cyclic amidine-functionalized polymers that were challenged by a stream of pure CO₂ (~0.34 mmol CO₂/g polymer).⁵⁷ This demonstrates the ability of our linear amidine-functionalized polymers to behave as effective CO₂ sorbents under very different CO₂ exposure conditions.

$$CO_2 \text{ uptake} = \frac{\text{Area} \times \text{flow rate} \times CO_2 \text{ concentration}}{\text{mass polymer}} \quad (1)$$

As expected, CO₂ adsorption decreases with decreasing amidine content, with the exception of copolymer **3f₁₃**. This inconsistency may be a result of solubility differences between the copolymers, which require different precipitation solvents for purification and isolation.

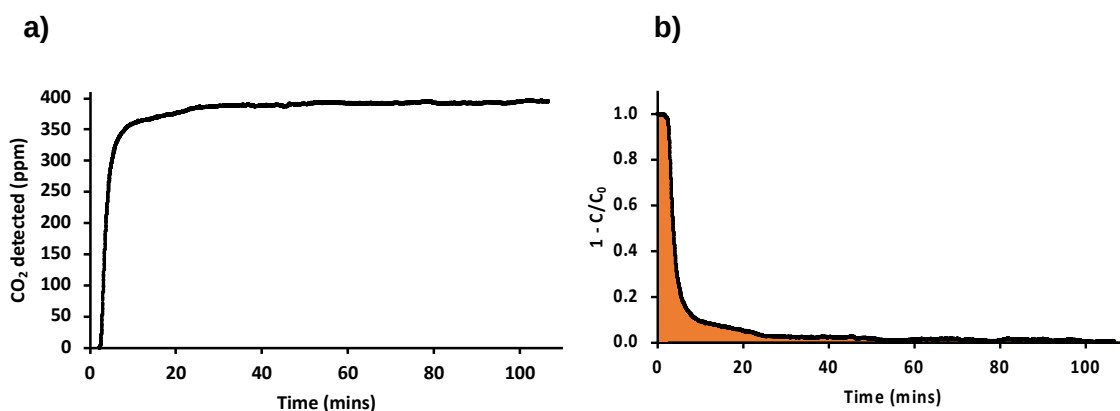


Figure 3.3. Data obtained from adsorption under DAC conditions. a) CO₂ detected (ppm) versus exposure time (mins). The CO₂ detected is divided by 400 ppm to obtain the C/C_0 concentration value that results in the plot b) $1 - C/C_0$ vs. time. The area under this curve is used to obtain the mass of CO₂ adsorbed per mass of polymer.

Table 3.2 CO₂ capture amounts for poly(St-*ran*-VBTAm) (**3**) copolymers under DAC conditions.

Copolymer	Sample Mass (mg)	Area Under Curve (min)	mmol CO ₂ /g polymer
3f₁₀₀	16.3	6.641	0.287
3f₅₆	16.1	5.460	0.239
3f₃₀	16.9	4.801	0.200
3f₁₃	16.2	4.909	0.214

This may introduce inconsistencies in the processing of the polymers and, as a result, copolymer **3f₁₃** features smaller particles size with a higher surface area-to-volume compared to the other copolymers. The finer particle size (granularity) of **3f₁₃** is seen in the optical microscopy images presented in **Figure C14** and **Figure 3.4**. Although we did not control for particle size and shape, these DAC experiments demonstrate that poly(St-*ran*-VBTAm) can capture CO₂ at atmospheric concentrations of CO₂ (400 ppm), and suggest that CO₂ adsorption capacity can be tailored by the degree of amidine functionalization. In addition and as expected, increased surface area-to-volume ratios enables better CO₂ uptake because it makes more amidine motifs available for capture.

3.4.1.4 Molecular Basis of CO₂ Binding.

Triazoles introduced into molecular organic frameworks (MOFs) have been shown to selectively capture CO₂.^{108,109} Therefore, to assess whether triazole groups in the poly(St-*ran*-VBTAm) copolymers participate in CO₂ capture, we used neutron vibrational spectroscopy and calculations based on density functional theory to gain insight into the binding of CO₂ with the amidine-functionalized polymers. Neutron vibrational spectroscopy (NVS) is an inelastic neutron scattering technique that probes molecular vibrations, which are sensitive to the chemical structure and local interactions. Because NVS measures the dynamics of nuclei, it is not restricted by selection rules in the same way as IR spectroscopy. The data obtained from NVS experiments for homopolymer **3f₁₀₀** are shown in **Figure 3.5**. The “blank” desorbed sample measured at 5 Kelvin is shown by the green curve and the CO₂-loaded sample measured at 27 °C is shown by the red curve. Unfortunately, prominent polymer backbone features are visible in the **3f₁₀₀** spectra, and these obscure the small spectral changes caused by CO₂ uptake. Although it would be ideal to use isotopically-substituted (deuterated) repeat units, another useful approach

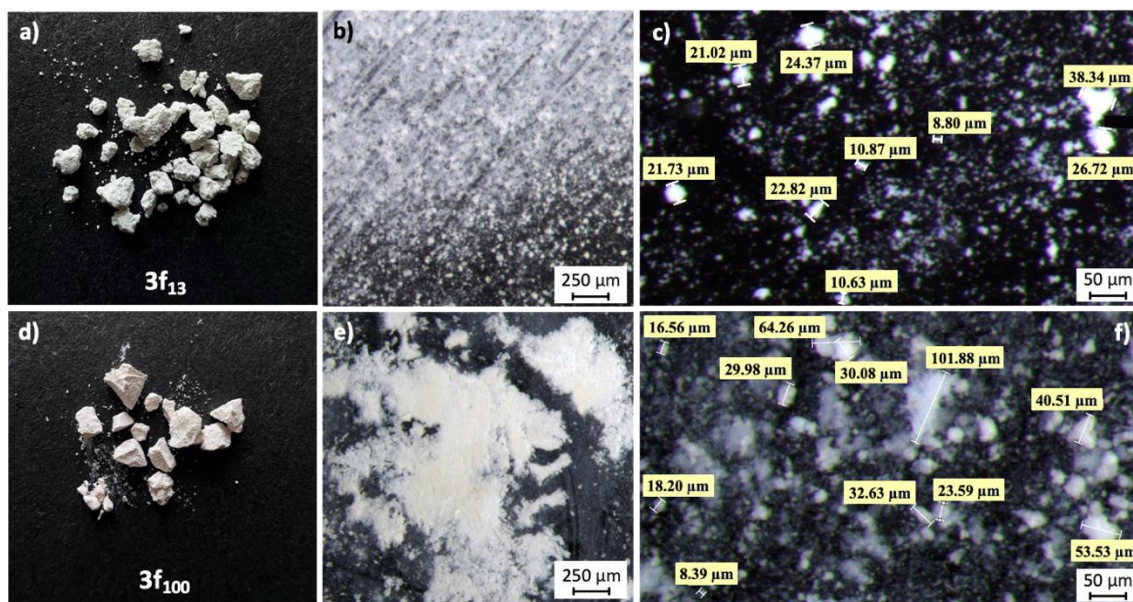


Figure 3.4. Optical images of copolymer $3f_{13}$ (a-c) and copolymer $3f_{100}$ (d-f) at various magnification levels. Images (a) and (d) were taken with a mobile device camera while images (b), (c), (e), and (f) were taken with an optical microscope. Smaller particle distributions are observed for copolymer $3f_{13}$.

is to subtract backbone signals by using a spectrum for pure polystyrene (PS) (orange curve). The resulting subtracted spectra shown by the blue curve (desorbed **3f₁₀₀**) and the pink curve (CO₂-loaded **3f₁₀₀**) help to enhance the vibration changes caused by CO₂ adsorption, that are already observable in the raw data.

DFT calculations performed on a dimer consisting of one styrene repeat unit and one amidine-functionalized repeat unit were used to interpret the NVS spectrum and identify the binding mode. Specifically, a mode consisting of one arrow at 654 cm⁻¹ in **Figure 3.5**. This is a complex mode involving out-of-plane deformation of the triazole ring coupled to a C-N=C (in-plane) deformation at the amidine nitrogen and strong wagging of the CO₂ molecule that features an average bending angle is 150°. This mode is calculated to have an energy of ~658 cm⁻¹ (expt. 654 cm⁻¹) for the CO₂-loaded dimer, and an energy of ~647 cm⁻¹ (expt. 638 cm⁻¹) in the same model without the CO₂ molecule. This shift is clearly observable in the VISION data, indicating that CO₂ adsorption does indeed occur at the amidine nitrogen. To corroborate the findings from these calculations, which show that the amidine N is responsible for CO₂ adsorption, an alkylated copolymer was synthesized by “clicking” 1-hexyne onto the copolymer scaffold (see **4** in Scheme 1). The resulting copolymer, **4f₅₆**, was subjected to CO₂ adsorption studies via TGA using a flow of pure CO₂. **Figure C13a** shows that the alkylated copolymer, **4f₅₆**, adsorbed very little CO₂ (~0.3 wt%), and that CO₂ was effectively released upon ramping the temperature to 50 °C. Similarly, **Figure C13b** shows that CO₂ adsorption by polystyrene was negligible (<0.1 wt%), as expected. Considered with the NVS data and DFT results, these studies clearly show that the linear amidine is the active motif for CO₂ capture, as the triazole linkage and styrenic repeat units contribute negligibly to CO₂ adsorption.

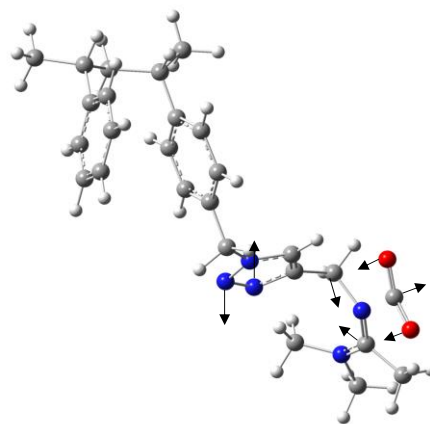
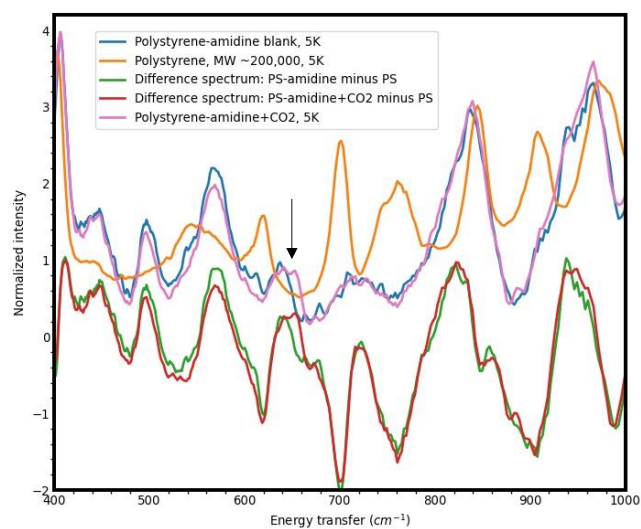


Figure 3.5. INS vibrational spectra (left) for the desorbed (green), CO₂-loaded (red), “PS-subtracted” desorbed (blue), and “PS-subtracted” CO₂-loaded (pink) experiments for the **3f₁₀₀** homopolymer. The model on the right is a result of DFT calculations showing the complex modes of motion represented by the signal at 654 cm⁻¹ in the INS vibrational spectra.

3.4.2 Examining Chemical Changes Due to Hydrolysis.

Amidine-functionalized polymers are reputed to be prone to insolubility and cross-linking reactions. Specifically, Endo et al.⁵⁰ and Ochiai et al.⁵⁶ proposed that amidinium ions form upon adsorption of CO₂ and result in cross-linking between cyclic amidine-functionalized styrenic polymers, resulting in insolubility in all common organic solvents except DMF. Similarly, Barkakaty et al. postulated that amide groups (which were a product of the ring-opening reaction to functionalize PVDMA with a modified THP) introduced hydrogen bonding interactions that led to physical cross-linking and insolubility in all common organic solvents.⁵⁷ In this work, it was observed that on the time scale of several days the linear amidine-containing copolymers hydrolyzed at ambient temperature due to atmospheric moisture, which rendered them insoluble. Therefore, it is relevant to examine how hydrolysis affects the chemical nature and physical properties of poly(St-*ran*-VBTAm) and the resulting impact on CO₂ adsorption capacity. To address these matters in part, the CO₂ adsorption capacity of the hydrolyzed copolymer, **3Hf**₅₆, was tested by exposure to a flow of pure CO₂ and monitoring changes in mass (by TGA). **Figure 3.6** shows that the maximum adsorption for **3Hf**₅₆ is only 1.70 wt%, which clearly demonstrates a dramatic loss of CO₂ adsorption capacity compared to **3f**₁₀₀, which featured an adsorption capacity of 22 wt%. This behavior is attributed to a loss of amidine functionality due to hydrolysis. It is worth noting that **3fH**₁₀₀ could not be synthesized due to solubility issues (as discussed later).

3.4.2.1 *Effect of Hydrolysis on the Thermomechanical Properties of Amidine-Functionalized Polymers.*

The thermomechanical properties of the amidine-functionalized (**3**) and the corresponding hydrolyzed (**3H**) copolymers were studied to observe changes in *T_g* and degradation behaviors -

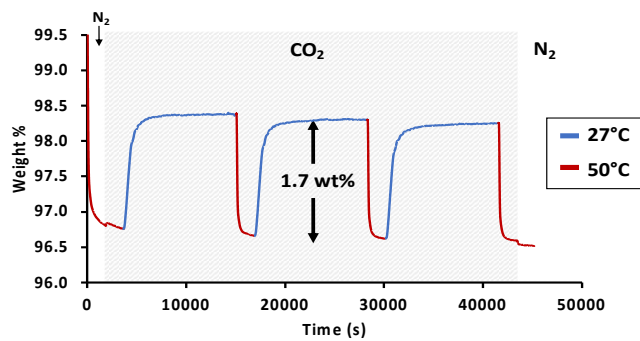


Figure 3.6. TGA profile that demonstrates the capture and release of CO₂ for the hydrolyzed copolymer (**3Hf₅₆**), where the chamber temperature is at either 27 °C (blue line) or 50 °C (red line). The sample is exposed to a gas flow of either CO₂ (shaded region) or N₂ (unshaded region) gas.

due to hydrolysis. The T_g values reported in **Figure 3.7** are based on mass composition (instead of mol%) of the copolymers for consistency with the Fox Equation (Eqn. 2). Note that copolymers of the same molar composition have different mass compositions due to chemical changes that occur upon hydrolysis of the amidine group. For amidine-functionalized copolymers (**3**), the trend of T_g decreasing with increasing amidine content is likely caused by an increase in free volume due to the bulky triazole and linear amidine motifs. However, as shown by the dotted line in **Figure 3.7**, the data show a positive deviation from ideal behavior. Huang et al.¹¹⁰ and Kuo et al.¹¹¹ state that this is a common behavior for copolymers containing affinity interactions (e.g. hydrogen bonding), which results in positive deviation from ideal behavior. In amidinefunctionalized polymers, these affinity interactions can come from intermolecular interactions between the highly polar amidine and triazole groups. Another source of affinity interactions for amidine-functionalized polymers described by Sakuragi et al.⁵⁸ and Furusho et al.^{112,113} is described the formation of amidinium-carboxylate salt bridges in the presence of carboxylate groups, or other functional groups such as amides that are capable of hydrogen bonding. The experimental T_g data for the amidine-functionalized copolymers was fitted to the Gordon-Taylor (G-T) equation, as described by Eqn 3, and an adjustable fitting parameter, K , was calculated by a linear regression. In order to adhere to the constraints of the G-T model, only a single experimental data point for copolymer **3f₁₃** was used in order to obtain an estimate of the K parameter. Specifically, the model requires that all copolymer T_g values fall within the bounds defined by the T_g values of the homopolymers, **3f₁₀₀** and polystyrene. For the amidine-functionalized copolymers, the trend is well described by $K = 4.0 \pm 0.3$, as shown in **Figure 3.7**. In comparison, the T_g values of the hydrolyzed copolymers are essentially constant across the composition range. This behavior is likely due to hydrogen bonding

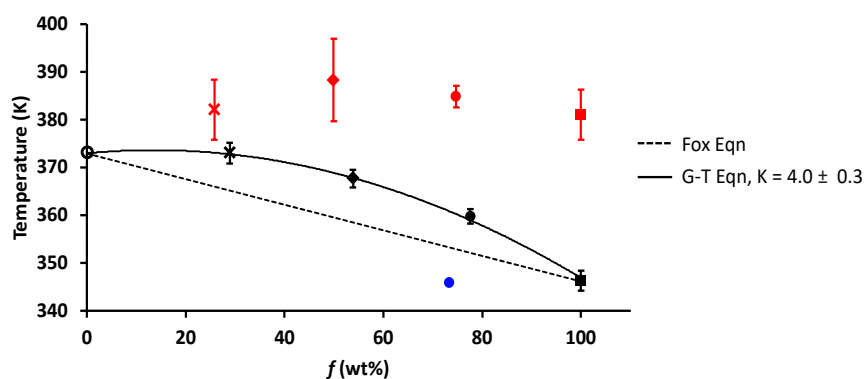


Figure 3.7. T_g values measured for amidine-functionalized copolymers (black data points) and hydrolyzed copolymers (red data points) as a function of copolymer composition, reported in weight %. The shapes of the data points indicate the copolymer composition on a molar basis: × (13 mol%), ◆ (30 mol%), ● (56 mol%), ■ (100 mol%). The T_g for an alkylated copolymer (bereft of the amidine functionality) poly(St-*ran*-StAlkyl) is also shown (blue ●), and the hollow circle corresponds to the T_g for polystyrene.

interactions between amide groups and physical cross-linking, which is consistent with all of the resulting copolymers, except **3f₁₃**, being insoluble in common organic solvents and water. This insolubility prevented complete hydrolysis of the amidine-functionalized homopolymer, **3f₁₀₀**, as evidenced from the ATR-FTIR, which will be discussed later. As a result, the T_g value is reported for **3f₁₀₀** represents a partially-hydrolyzed version.

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (2)$$

$$T_g = \frac{w_1 T_{g1} + K w_2 T_{g2}}{w_1 + K w_2} \quad (3)$$

Thermogravimetric analysis (TGA) was used to analyze the degradation patterns of the amidine-functionalized, hydrolyzed, and alkylated copolymers in a nitrogen atmosphere. As an example, **Figure 3.8a** shows the thermogram of the amidine-functionalized homopolymer, **3f₁₀₀**, (black trace) which demonstrates a multi-step degradation consistent with degradation behaviors for POSS nanoparticles functionalized with linear amidine groups as reported by Guerrero et al.¹¹⁴ This multi-step degradation becomes less apparent

with decreasing amidine content, and a higher char yield is observed for copolymers with higher amidine content. For all amidine-functionalized copolymers, the temperature range for amidine side group degradation is ~240-270 °C. Another degradation event is evident between 380-400 °C for copolymers **3f₁₀₀**, **3f₅₆** and **3Hf₅₆**. This is attributed to thermal degradation of the triazole linkage, and this is supported by results from Xue et al., who showed that poly(1,2,3-triazole) resins underwent thermal decomposition at ~400 °C.¹¹⁵ Although triazole degradation could not be seen clearly for **3f₃₀** and **3f₁₃** due to their lower number of triazoles, triazole degradation can be seen around 400 °C in the degradation behavior of the alkylated copolymer, **4f₅₆**, as shown in **Figure C12**. Finally, we observe that the hydrolyzed copolymer, **3Hf₅₆**, does not exhibit multi-

step thermal degradation, though it does show a feature at ~380 °C that is consistent with triazole degradation, as shown in **Figure 3.8b**.

3.4.2.2 Hydrolysis of the Small Molecule Analog of Amidine-Functionalized Polymers (3).

Small molecule analogs of the amidine-containing repeat units were used to assess the chemical consequences of hydrolysis, as determined by NMR spectroscopy (**Figure 3.9**, and **Figure C10**) and DART-MS (**Figure C11**). The synthesis of the amidine-functionalized small molecule analog, ((1-benzyl-1,2,3-triazole-4-yl)methyl)-N,N-dimethylacetamidine (“benzyl-TA”), and its subsequent hydrolysis to yield ((1-benzyl-1,2,3-triazol-4-yl)methyl)acetamide (“benzyl-TAH”) is detailed in the Supporting Information, and the ¹H NMR spectrums of these two compounds are shown in **Figure 3.9**. The spectra show the upfield shift of the methylene protons **f** → **f'** upon hydrolysis along with a change from a singlet (**f**) to a doublet (**f'**) due to the presence of the adjacent amide proton in the hydrolyzed small molecule. This amide proton (**i'**) appears at 6.11 ppm as a broad peak, which is characteristic of a proton that is capable of hydrogen bonding. The spectrum also shows the disappearance of the three methyl groups (**h** and **g**) and the appearance of a methyl group (**j'**) at 1.97 ppm, which falls within the expected range for -CCH₃ protons of N-methylacetamide.^{116,117} These transformations confirm the loss of amidine functionality and formation of a secondary amide group. ¹³C APT NMR analysis was used as an additional characterization tool to elucidate the structure of the small molecule analogs. Those spectrums, which are presented in **Figure C10**, distinguish carbons based on their multiplicity of attached protons and, in so doing, confirm the loss of methyls at the dimethyl amine terminus upon hydrolysis.

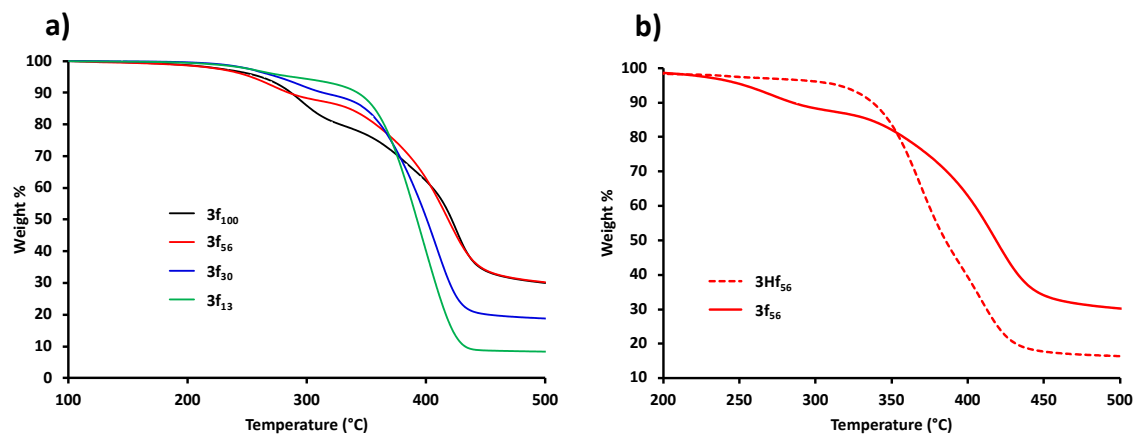


Figure 3.8. Overlaid TGA thermograms of a) amidine-functionalized copolymers $3f_{100}$ (black), $3f_{56}$ (red), $3f_{30}$ (blue), and $3f_{13}$ (green) and b) a comparison of the amidine-functionalized copolymer, $3f_{56}$, (solid red line) with the hydrolyzed copolymer, $3Hf_{56}$, (dashed red line).

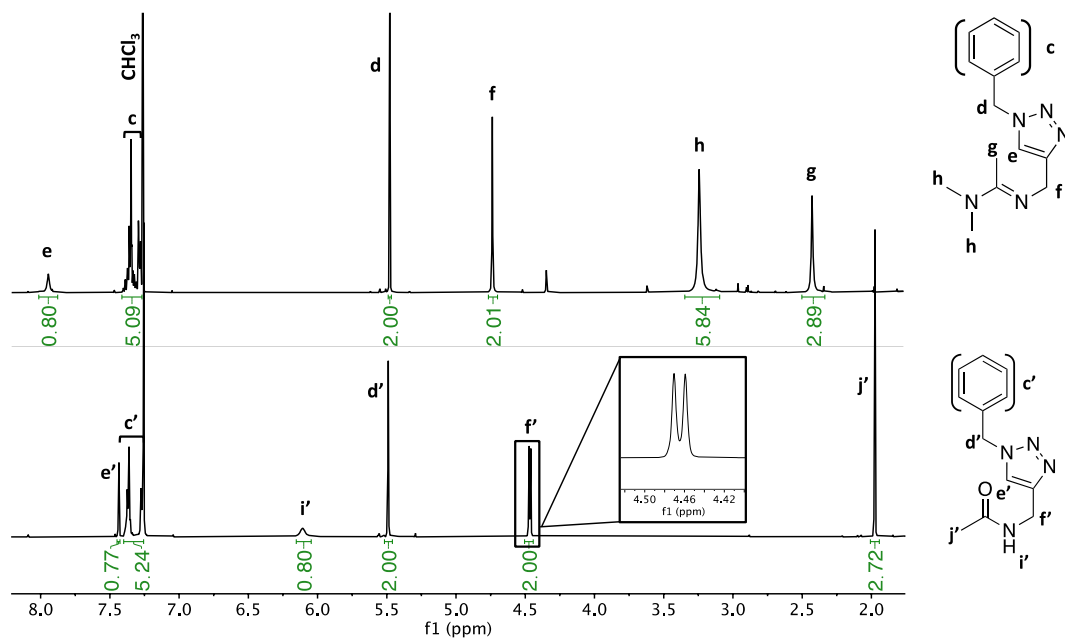


Figure 3.9 ^1H NMR spectra of benzyl-TA (top). ^1H NMR (500 MHz, 25°C , CDCl_3). δ , ppm: 2.41 (s, 3H, CH_3), 3.23 (s, 6H, CH_3), 4.73 (s, 2H, CH_2), 5.47 (s, 2H, CH_2), 7.26-7.40 (arom. CH of styrenic ring), 7.94 (s, 1H, CH of triazole). ^1H NMR spectra of benzyl-TAH (bottom). ^1H NMR (500 MHz, 25°C , CDCl_3). δ , ppm: 1.97 (s, 3H, CH_3), 4.47 (d, 2H, CH_2), 5.49 (s, 2H, CH_2), 6.11 (s, 1H, -NH of amide), 7.27-7.40 (arom. CH of styrenic ring), 7.43 (s, 1H, CH of triazole).

Finally, ATR-FTIR spectroscopy was used to confirm the chemical transformation of the amidine-functionalized polymer to its hydrolyzed form. Here we focused on the region from 1450-1750 cm^{-1} to encompass the range where Amide I and Amide II modes, which correspond to stretching of C=O groups and mixed vibrations due to N-H bending and C-N stretching in secondary amides,¹¹⁸ are observed. As seen in **Figure 3.10**, the spectrum for the hydrolyzed copolymer shows two stretches centered at 1650 cm^{-1} and 1541 cm^{-1} , indicative of Amide I and Amide II modes, respectively, along with a broad and significant signature at $\sim 3270 \text{ cm}^{-1}$ that is consistent with vibrational modes of the Amide A region (3300-3500 cm^{-1}). These Amide A modes are identified by Ji and coworkers,¹¹⁸ who reported six “fine components” obtained from the resonance structures of the protonated, hydrated, and hydroxylated products of N-methylacetamide. Using density functional theory, they determined that the Amide A region contains N-H stretching or bending vibrations of the amide group and the O-H stretching/bending vibrations resulting from the hydrated or hydroxylated N-methylacetamide.¹¹⁸ They contend that the peaks in the 3000-4000 cm^{-1} range for amides are from the fine components of the amide group, not free water molecules.¹¹⁸

The amidine-functionalized copolymer (black line) has one distinct mode at 1611 cm^{-1} , which assigned to C=N stretching of the amidine motif. To confirm that this stretch is in fact assigned to the amidine, we also acquired an ATR-FTIR spectrum of PDAA (the small molecule containing the linear amidine). The stacked spectra of PDAA and the amidine-functionalized copolymer shown in **Figure C9** shows that the C=N modes are present in both compounds at 1611 cm^{-1} .

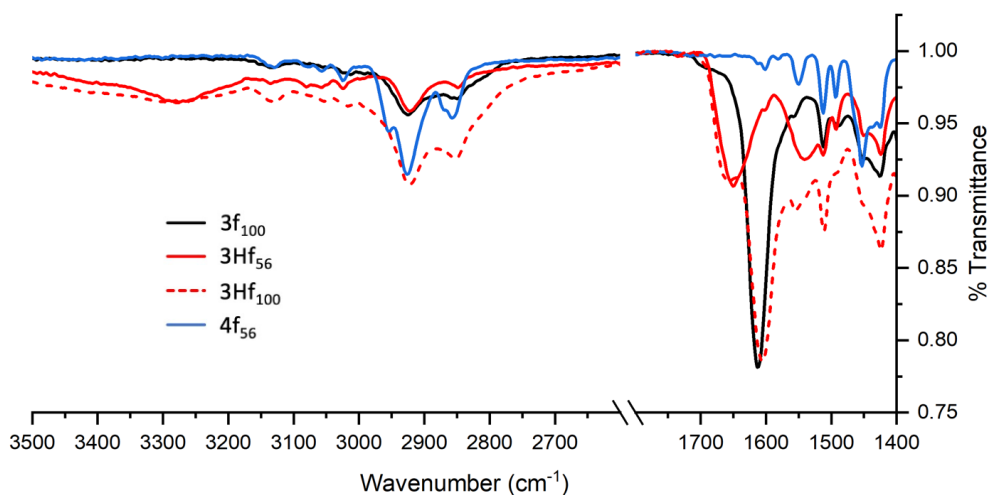


Figure 3.10. ATR-FTIR spectra in the 3500-2700 cm^{-1} region and 1750-1400 cm^{-1} region for copolymers **3f**₁₀₀ (black), **3Hf**₅₆ (red), **3Hf**₁₀₀ (dashed red) and **4f**₅₆ (blue). The amidine-functionalized polymer, **3f**₁₀₀, has a signature stretch at 1611 cm^{-1} attributed to the C=N stretching of the amidine motif. The hydrolyzed copolymers, **3Hf**₅₆ and **3Hf**₁₀₀, show two new stretches (1541 and 1650 cm^{-1}) that are attributed to the Amide II and Amide I vibrational modes. The Amide A mode is also seen (at 3274 cm^{-1}) in the spectra of the hydrolyzed copolymers. The alkylated copolymer, **4f**₅₆, illustrates the absence of both amidine and amide functionality in the 1450-1750 cm^{-1} range. Copolymer **3Hf**₅₆ shows no indication of amidine functionality (stretch at 1611 cm^{-1}), while copolymer **3Hf**₁₀₀ clearly has remaining amidine functionality due to the copolymer becoming insoluble before complete hydrolysis.

3.5 Conclusions

We have probed the ability of poly(St-*ran*-VBTAm) copolymers to reversibly capture and release CO₂ in both concentrated (pure CO₂) and ultra dilute regimes (direct air capture) and analyzed physical and chemical consequences of hydrolysis side reactions. The maximum CO₂ adsorption capacity for the amidine-functionalized homopolymer, **3f**₁₀₀, is 22 wt%, which is comparable to the performance of leading porous organic polymers. The CO₂ adsorption capacity can be tailored by altering the copolymer composition to control the degree of amidine functionalization which offers advantages as far as ease of processing. In addition, neutron vibrational spectroscopy and density functional theory calculations informed the location of binding for CO₂ at the amidine motif. An “amidine-lacking” copolymer equivalent, poly(St-*ran*-VBTB), corroborated these results by demonstrating negligible CO₂ binding at the triazole group. Finally, we demonstrated that hydrolysis of the amidine-functionalized copolymers yields amide functionality and results in a large reduction of CO₂ adsorption capacity (1.7 wt%). Studies of the thermal properties of the hydrolyzed copolymers suggest that insolubility is driven by hydrogen bonding interactions between the amide functional groups, which resulted in an increased T_g and complete insolubility at the highest amidine content. Overall, this work contributes important insights on the physical and chemical properties, behaviors, and limitations of amidine-functionalized copolymers and their application as solid sorbents for CO₂ capture systems.

APPENDIX C

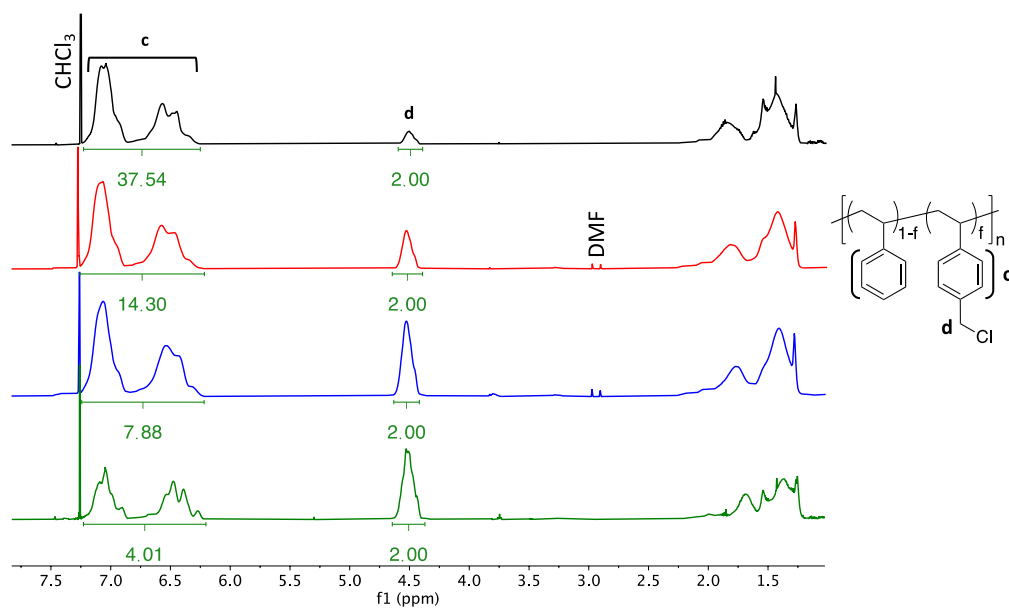


Figure C1. Stacked ^1H NMR spectra of poly(St-ran-VBC) at various copolymer ratios: **1f₁₃** (black), **1f₃₀** (red), **1f₅₆** (blue), and **1f₁₀₀** (green). ^1H NMR (500 MHz, 25 °C, CDCl_3). δ , ppm: 1.22-2.28 (CH and CH_2 of polymer backbone), 4.51 (s, 2H, CH_3), 6.24-7.24 (arom. CH of styrenic ring).

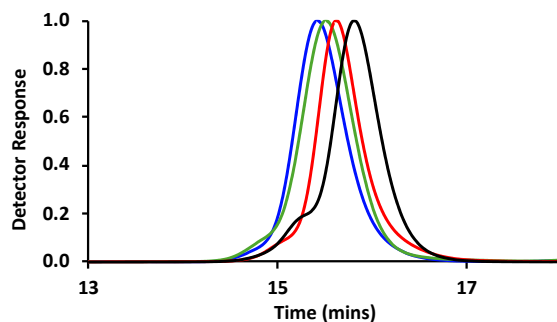


Figure C2. Molecular weights and dispersity were obtained using conventional calibration analysis from GPC traces of poly(St-*ran*-VBC) of various compositions. **1f₁₃** (black): $M_n = 10.2$ kg/mol, $\bar{D} = 1.15$; **1f₃₀** (red): $M_n = 11.0$ kg/mol, $\bar{D} = 1.14$; **1f₅₆** (blue): $M_n = 14.1$ kg/mol, $\bar{D} = 1.11$; and **1f₁₀₀** (green): $M_n = 13.2$ kg/mol, $\bar{D} = 1.14$.

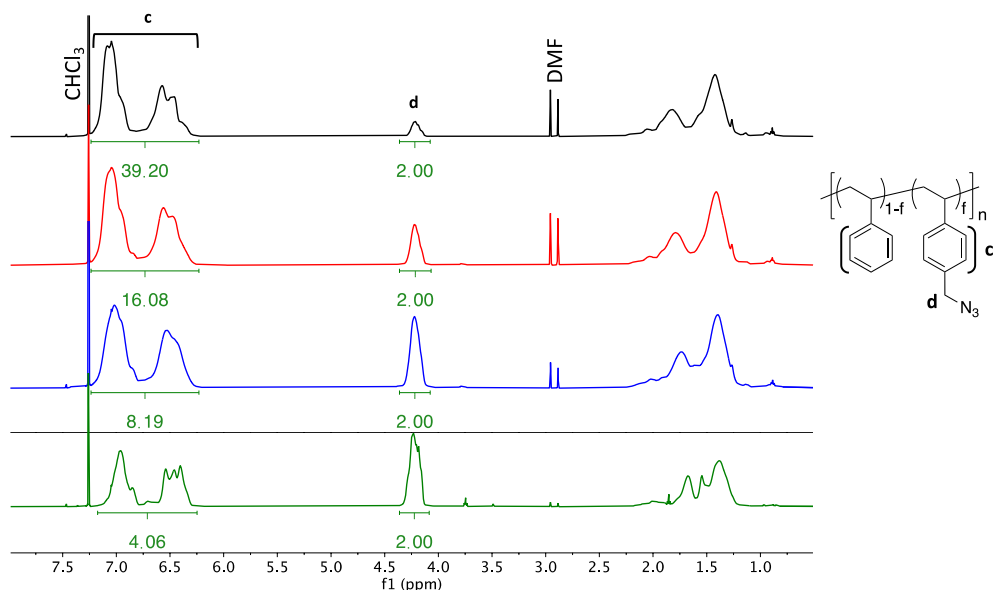


Figure C3. Stacked ^1H NMR spectra of poly(St-*ran*-VBA) at various copolymer ratios: **2f₁₃** (black), **2f₃₀** (red), **2f₅₆** (blue), and **2f₁₀₀** (green). ^1H NMR (500 MHz, 25 °C, CDCl_3). δ , ppm: 1.08-2.23 (CH and CH_2 of polymer backbone), 4.22 (s, 2H, CH_2), 6.26-7.23 (arom. CH of styrenic ring).

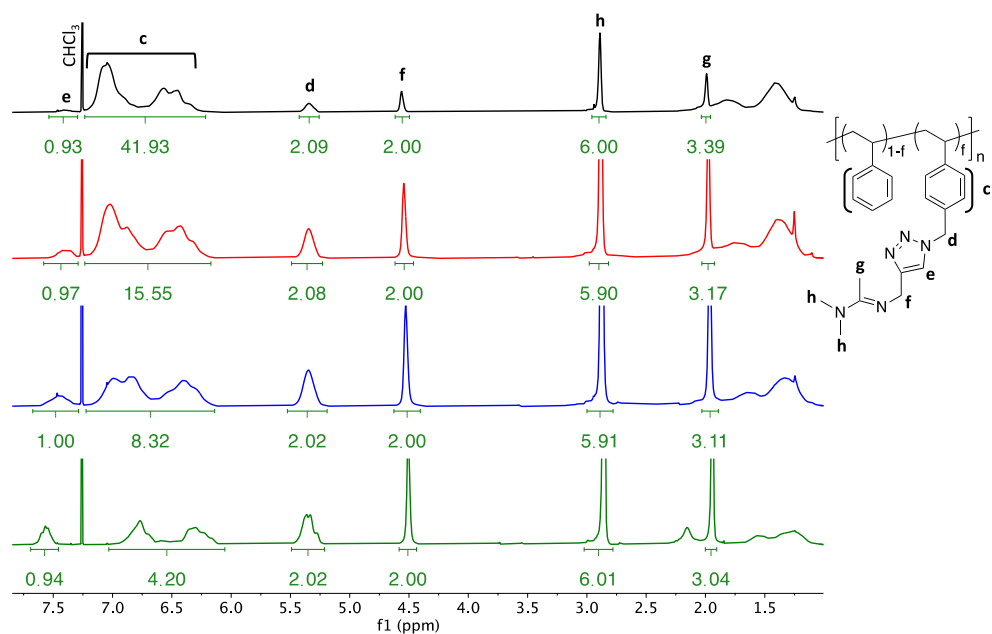


Figure C4. Stacked ^1H NMR spectra of poly(St-*ran*-StAm) at various copolymer ratios: **3f₁₃** (black), **3f₃₀** (red), **3f₅₆** (blue), and **3f₁₀₀** (green). ^1H NMR (500 MHz, 25 °C, CDCl_3). δ , ppm: 1.06-1.87 (CH and CH_2 of polymer backbone), 1.96 (s, 3H, CH_3), 2.88 (s, 6H, CH_3), 4.53 (s, 2H, CH_2), 5.35 (s, 2H, CH_2), 6.14-7.17 (arom. CH of styrenic ring), 7.30-7.61 (s, 1H, triazole CH).

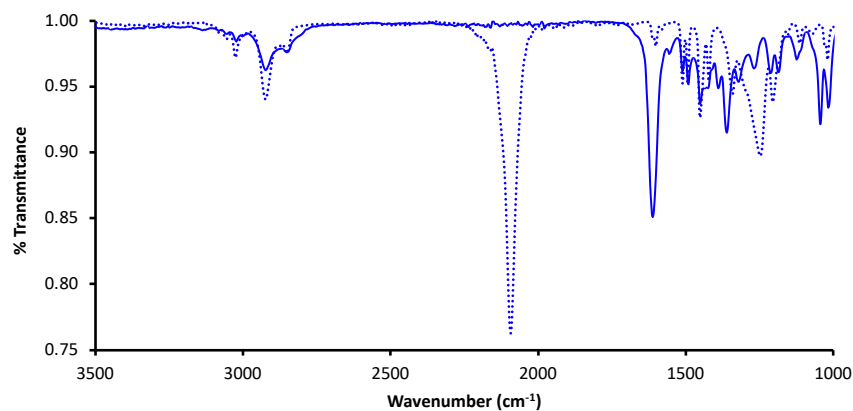


Figure C5. ATR-FTIR spectra of copolymer **2f₅₆** (dotted blue line) and copolymer **3f₅₆** (solid blue line). The disappearance of the azide stretch at 2103 cm⁻¹ and the appearance of the amidine stretch at 1611 cm⁻¹ confirms successful conversion by the CuAAC “click” reaction. Spectra were acquired for 64 scans at a resolution of 4 cm⁻¹.

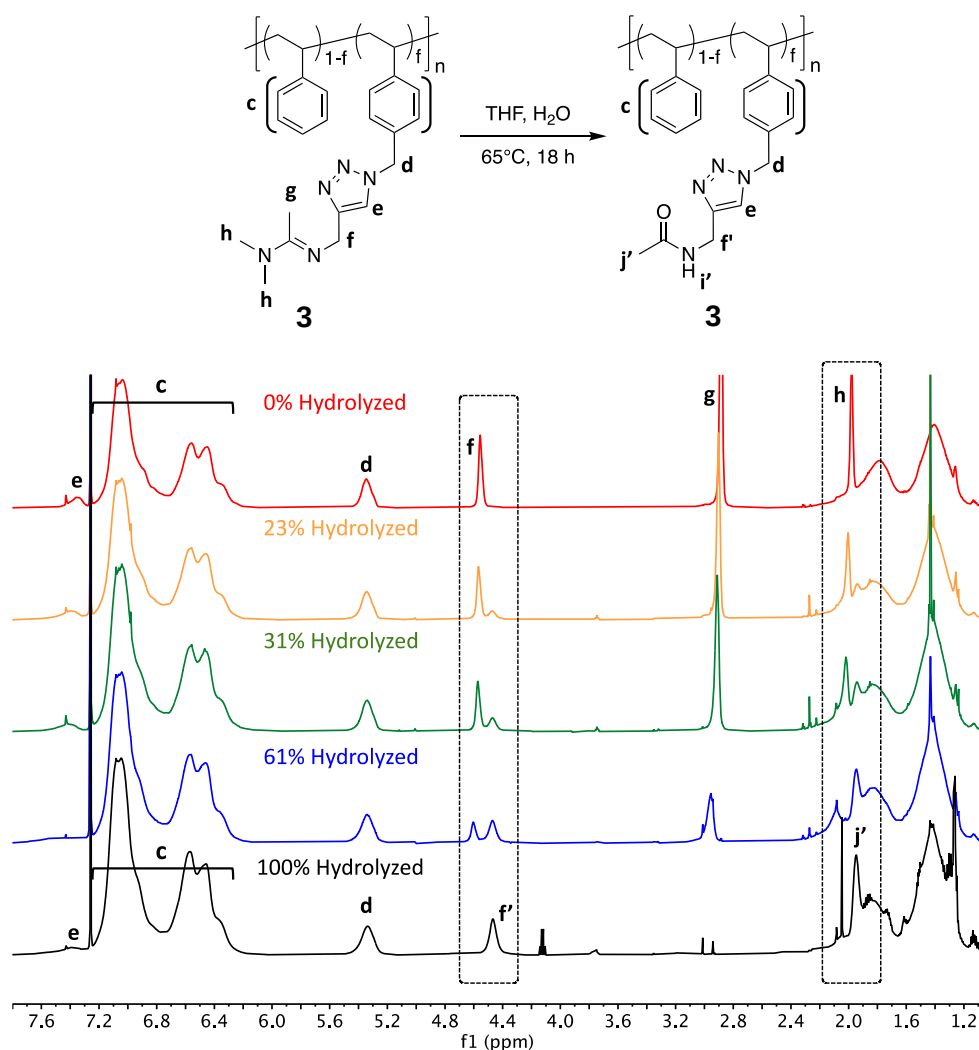


Figure C6. ¹H NMR analysis of copolymer hydrolysis (500 MHz, 25 °C, CDCl₃). Aliquots were taken to track the hydrolysis of the amidine-functionalized copolymer (**3f₁₃**). The proton shifts for the parent copolymer, **3f₁₃**, (red spectrum) and the hydrolyzed copolymer, **3hf₁₃**, (black spectrum) are labeled with peak assignments. Peaks **f** and **f'** were used to calculate the degree of hydrolysis. For copolymer **3hf₁₃**: δ, ppm: 1.95 (s, 3H, CH₃), 4.46 (s, 2H, CH₂), 5.34 (s, 2H, CH₂), 6.17-7.24 (arom. CH of styrenic ring), 7.29-7.61 (s, 1H, triazole CH).

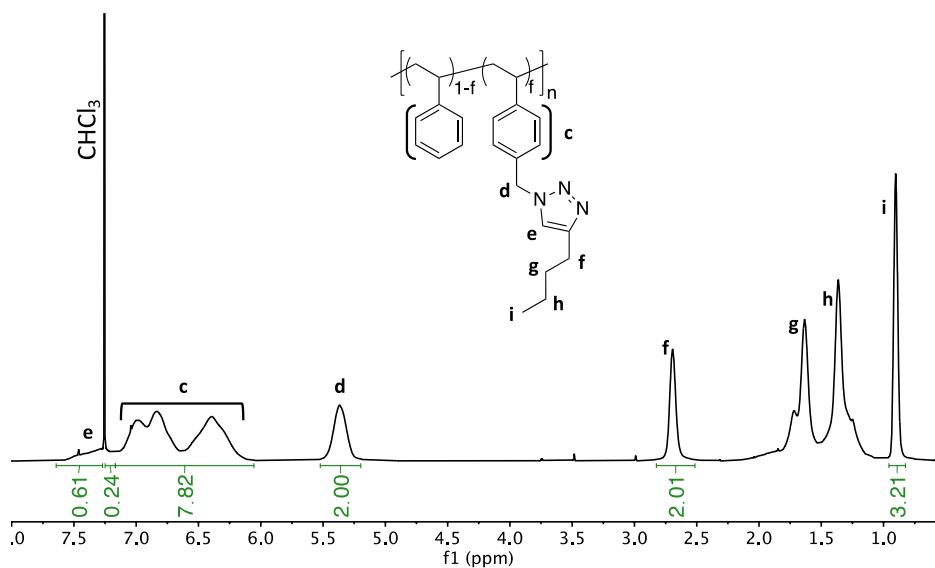


Figure C7. ^1H NMR spectra of poly(St-*ran*-StAlkyl), **4f₅₆**. ^1H NMR (500 MHz, 25 °C, CDCl_3). δ , ppm: 0.90 (s, 3H, CH_3), 1.36 (s, 2H, CH_2), 1.64 (s, 2H, CH_2), 2.70 (s, 2H, CH_2), 5.36 (s, 2H, CH_2), 6.10-7.16 (arom. CH of styrenic ring), 7.32-7.54 (s, 1H, triazole CH).

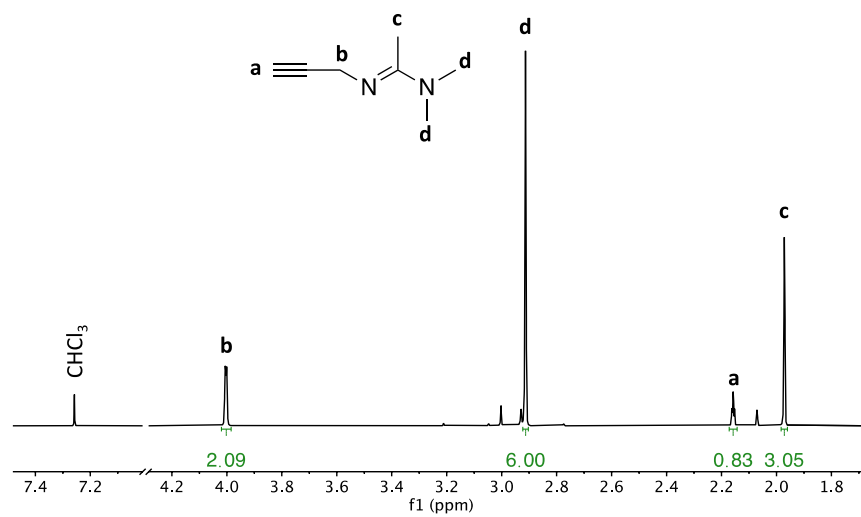


Figure C8. ^1H NMR of PDAA in CDCl_3 . ^1H NMR (500 MHz, 25 $^\circ\text{C}$, CDCl_3). δ , ppm: 1.97 (s, 3H, CH_3), 2.16 (t, 1H, CH), 2.91 (s, 6H, CH_3), 4.00 (d, 2H, CH_2).

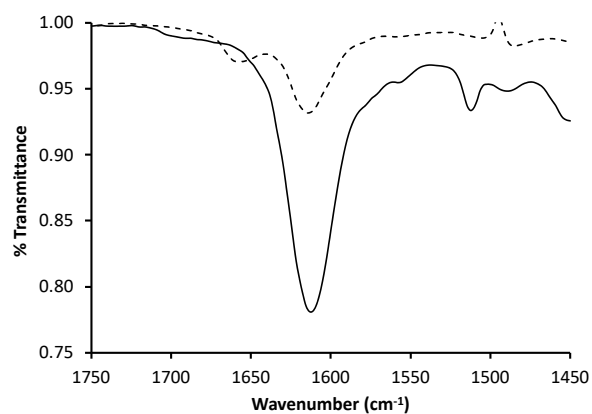


Figure C9. ATR-FTIR spectra of PDAA in the 1450-1750 cm⁻¹ region (dotted line) and the amidine-functionalize homopolymer, **3f₁₀₀** (solid line). The peak at 1611 cm⁻¹ corresponds to the C=N stretching mode of the amidine functional group, indicating that the amidine group is retained after the “clicking” PDAA onto the homopolymer using CuAAC.

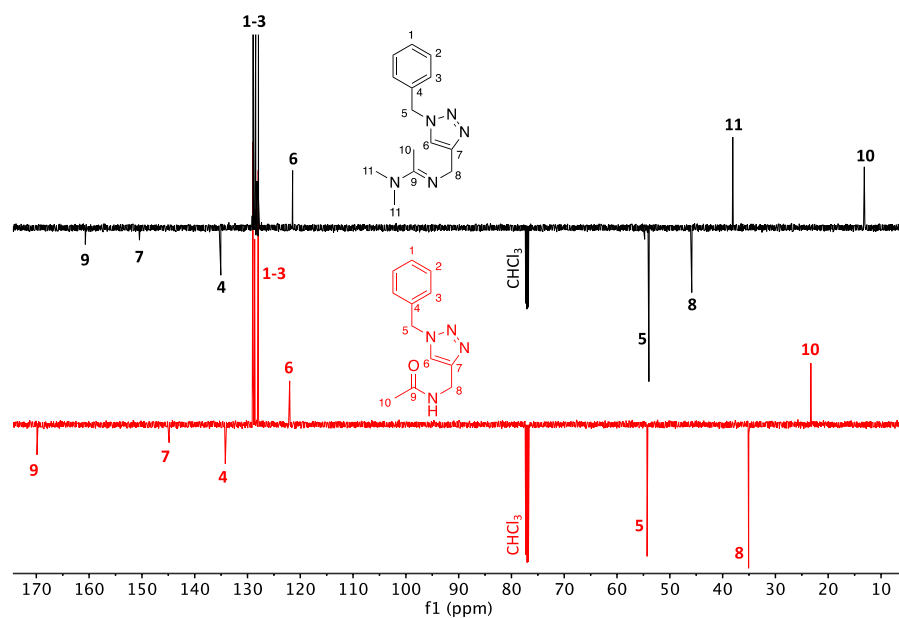


Figure C10. Stacked APT ^{13}C NMR spectra (500 MHz, 25 $^{\circ}\text{C}$, CDCl_3). Benzyl-TA (top): δ , ppm: 13.16, 38.09, 45.85, 53.96, 121.45, 127.91, 128.47, 135.06, 150.46, 160.72. Benzyl-TAH (bottom): δ , ppm: 23.28, 35.11, 54.41, 122.35, 128.33, 129.02, 129.33, 134.61, 145.30,

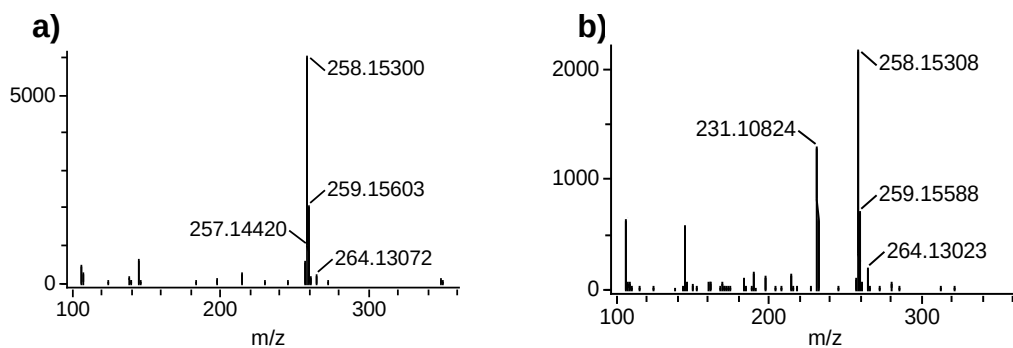


Figure C11. DART-MS in positive ion mode for the isolated "benzyl-TA" and the crude mixture resulting from partial hydrolysis of "benzyl-TA". HRMS for "benzyl-TA": calc'd $[M+H]^+$: 258.3640, found: 258.1530. HRMS for "benzyl-TAH": calc'd $[M+H]^+$: 231.2614,

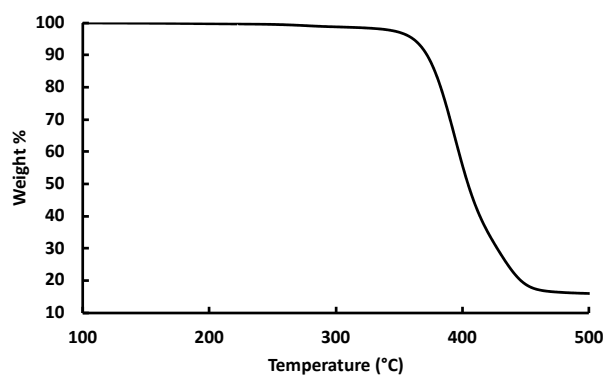


Figure C12. TGA thermogram of the alkylated copolymer, poly(St-ran-VBTB), **4f**₅₆. Degradation starts at ~350 °C and an inflection point at ~400 °C suggests a second degradation event that is likely indicative of triazole degradation.

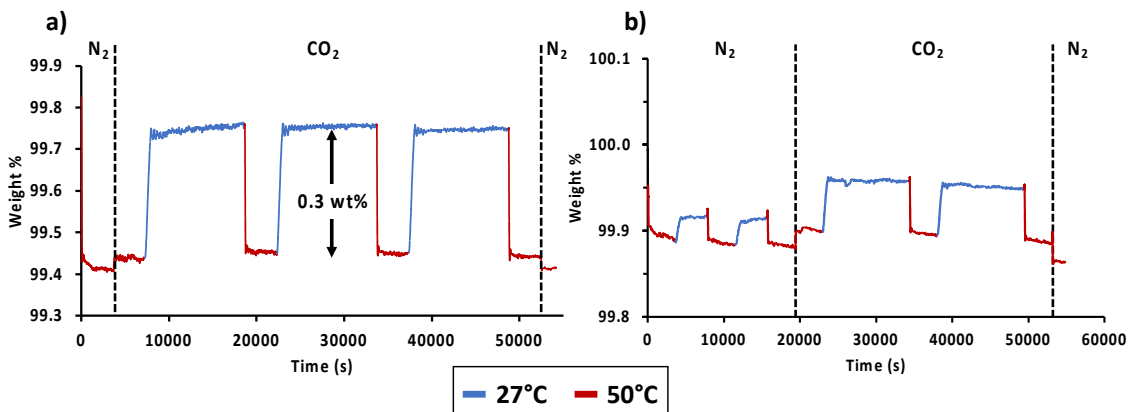


Figure C13. CO₂ adsorption behavior of (a) the alkylated copolymer, **4f₅₆**, and (b) a polystyrene standard. Adsorption occurs at 27 °C (blue line), while desorption occurs at 50 °C (red line). The dotted lines represent changes in gas flow between N₂ and CO₂. The alkylated copolymer, **4f₅₆**, has a CO₂ adsorption of 0.3 wt% while the polystyrene standard has a CO₂ adsorption of < 0.1 wt%.

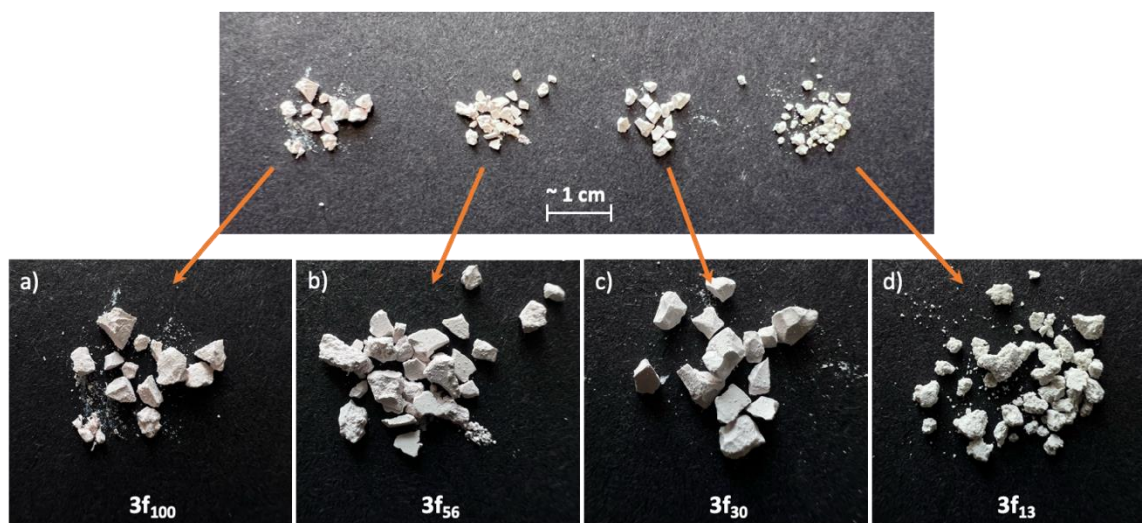


Figure C14. Optical images of the amidine-functionalized copolymer powders a) **3f₁₀₀**, b) **3f₅₆**, c) **3f₃₀**, and d) **3f₁₃**. Increased brittleness due to higher styrene composition results in a flakier texture and smaller particle size distribution for **3f₁₃**, resulting in higher surface area.

CHAPTER IV
CONCLUSIONS, SUMMARY AND FUTURE WORK

4.1 Conclusions and Summary

This dissertation has advanced the understanding of amidine-functionalized polymers through exhaustive investigations of their physical and chemical behaviors, including polymers containing the monocyclic amidine moiety, THP, and linear amidine-functionalized copolymers, which are referred to as poly(St-*ran*-VBTAm). Chapter II highlights efforts to functionalize acrylate- and styrene-based monomers with THP. These chemistries present unintended side reactions, such as aza-Michael addition at α,β -unsaturated carbonyl groups, double substitution of THP (which can only be mitigated by an excessively high stoichiometric ratio of THP to VBC), and hydrolysis of the THP when exposed to heat and moisture. These challenges revealed that THP is not a stable moiety due to its inherent nucleophilicity and sensitivity to hydrolysis that both contribute to the insolubility of the copolymers. In addition, the inability to polymerize the neutral THPSt monomer means that THP-modification of copolymers must proceed by a post-polymerization modification. One approach to this, which used the KI-catalyzed substitution reaction (Finkelstein reaction), results in incomplete conversion of reactive sites to THP. Chapter III describes in detail the physical and chemical responses of poly(St-*ran*-VBTAm) to exposure to CO₂ as well as other external stimuli, such moisture and temperature. These linear amidine-functionalized polymers demonstrated greater resistance to hydrolysis and increased solubility compared to the THP-functionalized polymers described in Chapter II. Despite previous works demonstrating that linear amidine small molecules in solution do not have good CO₂ adsorption capabilities,³⁴ we found that the CO₂ adsorption capacity of the linear amidine-functionalized homopolymer, **3f₁₀₀**, is competitive with the top-performing porous organic polymers. **3f₁₀₀** adsorbs 5.28 mmol CO₂/g polymer (or 22 wt%) when exposed to a flow of pure CO₂, and adsorbs 0.287 mmol CO₂/g polymer when exposed to a flow of CO₂ at atmospheric concentrations. In addition, the capture/release

experiments revealed that up to 91% of captured CO₂ can be desorbed solely by switching to an inert gas flow while maintaining the temperature at 27 °C. Furthermore, the combination of DFT calculations and NVS was used to identify the nanoscopic changes associated with CO₂ binding. These experiments, though preliminary, enabled us to ascertain the specific location of CO₂ binding, which occurred at the amidine functional group, through changes in vibrational modes.

Finally, our experimental observations of solubility changes inspired a full characterization of linear amidine-functionalized copolymers that were exposed to water (humidity). These studies revealed that hydrolysis of the linear amidine yields a secondary amide group. These changes trigger a large reduction in CO₂ adsorption capacity due to the loss of amidine functionality, and cause network formation (likely due to physical crosslinking) through the amide groups. This formation of a network is supported by the lack of solubility for all hydrolyzed copolymers, except **3f₁₃**, which has the highest styrene content (lowest amidine content). In addition, the hydrolyzed copolymer exhibit higher T_g values compared to the amidine-functionalized copolymers. These investigations highlight the chemical transformations of poly(*St-ran*-VBTAm) copolymers as a result of hydrolysis, which directly influences the physical properties of the copolymers as well as the CO₂ adsorption capacity. These studies offer compelling insight to the CO₂ capture and release of linear amidine-functionalized polymers, which could lay the groundwork for the amidine-functionalization of more complex constructs, such as polymer-grafted nanoparticles, functionalized porous materials or membranes, and more. These systems may offer better control over processability and surface area, which could result in more efficient materials for CO₂ capture. To enhance the impact of this dissertation research, we will described potential avenues for further research. This includes a reflective examination of potential improvements as well as insights into future outlooks and applications.

4.2 Future Work

As mentioned in Chapter II, the Mitsunobu reaction could have been improved by a more suitable pairing of the ligand and azo reagent, and by using an excess of THP to relative to the number of alcohol sites. ^1H NMR studies suggest that the Mitsunobu reaction can proceed under optimized conditions, however, the prevalence of the aza-Michael Addition side reaction under these conditions remains untested. Assuming that optimized Mitsunobu reaction conditions can be found to significantly promote condensation between THP and the alcohol (lacking an α,β -unsaturated carbonyl group), these conditions could be utilized in a post-polymerization modification approach to create THP-functionalized polyacrylates, which may broaden the types of constituent monomers that can be used to tailor copolymer properties. However, any unreacted hydroxyl groups remaining from incomplete coupling would likely promote the formation of amidinium-carboxylate salt bridges, which would lead to crosslinking between chains and induce solubility issues. Additionally, the presence of water is also a concern in the post-polymerization modification Finkelstein reactions described in Section 2.4.3. For instance, **Figure 2.12b** suggests that some of the THP moieties hydrolyze during the Finkelstein reaction. This is most likely due to the presence of water in DMF, since DMF is hygroscopic. Future care to ensure dry DMF is used in these reactions could prevent ring-opening of the THP motif, which would improve solubility characteristics of the copolymer and retain more THP groups for subsequent CO_2 capture.

Barkakaty et al. reported high conversion for the THP-functionalization of poly(2-vinyl-4,4-dimethylazlactone) (PVDMA), where 4-(N-methyltetrahydropyrimidine)benzyl alcohol (PBA) attacks via ring-opening of the azlactone ring in PVDMA to yield the PVDMA-PBA conjugate. However, the polymer suffered from solubility issues due to the presence of amide linkages in

PVDMA-PBA that promoted crosslinking by hydrogen bonding interactions. For future work, it would be worthwhile to explore how these crosslinking interactions could be disrupted by the introduction of alkyl substituents to improve the overall solubility of the polymer system. To achieve this, alkanol groups (such as 1-octanediol) could be introduced at the functionalization step simultaneously with PBA, where the composition of the resulting copolymer could be controlled by the ratio of alkanol to PBA. This approach may result in improved solubility characteristics while also retaining the high CO₂ adsorption capacity of the THP motif. In this pursuit, it would be appropriate to synthesize copolymers having various composition ratios (of alkanol to THP) to determine the optimal ratio that provides both high CO₂ adsorption and good solubility. This series of experiments would contribute insights into how to overcome solubility issues that are commonly seen in THP-functionalized polymers.

An additional project that could advance the findings in this dissertation would be to investigate the incorporation of CO₂-philic functional groups, such as oligo(ethylene glycol) (OEG), into the THP-functionalized copolymers to enhance the CO₂ adsorption capacity. Although there have been previous works along this line, those studies either involved mechanically blending poly(ethylene glycol) (PEG) with the amidine-functionalized polymer,⁶¹ creating an amidine-functionalizing a monomer containing a short OEG chain (so that the OEG and amidine always exist as a 1:1 ratio),⁶⁰ or applying binding organic liquids (BOLs).¹¹⁹ Instead, and for similarity to the linear amidine containing polymer that is derived from 4-vinylbenzyl chloride, it is proposed to create an OEG-containing monomer, 1-((2-(2-ethoxyethoxy)ethoxy)methyl)-4-vinylbenzene (EE-4-VB) as a styrene-based comonomer. This OEG-containing monomer offers the potential to be copolymerized with monomers used in this dissertation by free radical copolymerization. Two possible copolymerizations are offered here: 1) EE-4-VB could be

copolymerized with the protonated monomer, THPSt-HCl, by a water-based free-radical polymerization in a modified procedure similar to Sakuragi et al.,⁶¹ or 2) EE-4-VB could be copolymerized with benzyl azide followed by “clicking” the linear amidine, PDAA, by a CuAAC post-polymerization modification to create linear-amidine containing copolymers. A concern with the first option is that although monomers containing ethylene oxide are often water-soluble, an aqueous polymerization might make the removal of water from the system difficult. Furthermore, long exposure to water and elevated temperatures may result in hydrolysis of the amidines. Swager et al. have reported that attempts to create homopolymers with OEG-containing repeat units resulted in an insoluble polymer network due to the hygroscopic nature of OEG and their tendency to form gels.⁶⁰ Instead, the OEG-containing monomer was copolymerized with 4-vinylpyridine (4-VP) to achieve copolymers with a 1 : 10 molar composition of OEG : 4-VP. Copolymers with higher OEG composition resulted in an insoluble polymer network.

For this reason, the second option seems more practical due to the use of organic solvents, rather than water. A copolymer comprised of EE-4-VB and benzyl azide that is subsequently modified by a high-yielding “click” reaction to install the amidine functionality would allow copolymer composition to be controlled. However, the OEG- and amidine-containing repeat units would be drastically different in their physical and chemical properties, which likely means that copolymer properties would vary widely depending on the comonomer ratio. For example, because low molecular weight poly(ethylene glycol)s have a T_g below room temperature, copolymers having a higher OEG composition would likely feature a lower T_g , potentially resulting in polymers that are viscous at near-ambient temperatures and processability issues. In addition, while EO units have the potential to increase the CO₂-philicity of the system, they also have the potential to drastically affect the physical properties of the copolymers and increase their hygroscopic

character, creating issues due to hydrolysis of the amidine motifs and increase inter- and intra-chain interactions that compromise solubility. Thus, studies to explore and optimize OEG-content in amidine copolymers need to be mindful of such trade-offs.

As mentioned in Chapter III, direct air capture (DAC) experiments were used to measure the ability of various poly(*St-ran*-VBTAm) copolymers to adsorb CO₂ in conditions that mimic atmospheric concentration (400 ppm CO₂). Preliminary measurements suggest that CO₂ adsorption capacity is enhanced in the presence of water. For example, copolymer **3f₅₆** was purged with dry helium at slightly elevated temperature (50 °C) to remove all bound gases and water from the sample and then exposed to a flow of CO₂ at 5% humidity. The sample captured 0.504 mmol CO₂/g copolymer under humid conditions, but only 0.239 mmol CO₂/g copolymer when exposed to a dry flow of CO₂ gas. Although a variety of studies indicate that water is necessary for amidines to capture CO₂ (in the form of amidinium bicarbonate), some amidines can capture CO₂ as a zwitterionic carbamate in dry environments. Therefore, CO₂ adsorption measurements performed at various humidity levels would provide insight into the optimal humidity to achieve high CO₂ adsorption efficiency. These experiments can be completed on the DAC system used in this dissertation research, as it is equipped with a humidity controller. (Ancillary measurements would be needed to assess the extent of hydrolysis under those conditions.)

In addition, although DAC experiments revealed a general trend of decreasing CO₂ adsorption with decreasing amidine content, copolymer **3f₁₃** deviated from that trend: It exhibited a higher CO₂ adsorption capacity than copolymer **3f₃₀**. This is assumed to be related to different surface area-to-volume characteristics of the powders. It was observed that varying the copolymer composition resulted in powders having different particle sizes and granularity, which is likely a result of differences in solubility or having used different solvents to precipitate copolymers of

different amidine composition. As described in Chapter III, the solid powder obtained from copolymer **3f₁₃**, which had the lowest amidine-content, had finer particle sizes, which likely resulted in a higher surface area. This could explain why CO₂ adsorption for **3f₁₃** was higher than that of **3f₃₀**. It may be appropriate and useful to quantify the surface area of the powders produced from the various copolymers by Brunauer-Emmett-Teller (BET) surface area analysis. However, it may also be worthwhile to explore different processing methods to ensure more consistent powder granularity (surface area-to-volume ratios) across the various copolymers such as coating small particles (micron sized silica or mesoporous silica) by stirring them in a solution containing the copolymer. The amount copolymer deposited on the particle could be determined by monitoring mass loss at high temperatures using thermogravimetric analysis. This fixed support would likely eliminate or greatly reduce the difference in surface area-to-volume ratio across different samples.

Another objective for Chapter III was to study the molecular basis of CO₂ binding for amidine-functionalized copolymers by using a combination of DFT calculations neutron vibrational spectroscopy (NVS) to identify modes of CO₂ binding at the amidine. However, the NVS data are complicated by spectral overlap with modes associated with backbone and low resolution at the modes of interest. Although background subtraction and various data reduction methods were used to sharpen the modes of interest, it would be beneficial to alleviate these obstacles by preparing and using an isotopically-substituted (deuterium for hydrogen) copolymer. Deuterating the styrenic portions of the macromolecule would allow a higher resolution spectra to be obtained. To do this, deuterated styrene (styrene-d₈, which is commercially available) would be copolymerized with deuterated 4-VBC (which would have to be synthesized). This isotopically-substituted copolymer could be functionalized through the azide substitution and CuAAC “click” reactions as

discussed in Chapter III to create the linear amidine-containing copolymer. The isotopic substitution would eliminate signals in the NVS spectrum from aryl rings and backbone, resulting in a higher resolution NVS spectrum that captures the interaction and changes in vibrational modes of the amidines (and, potentially, the triazoles) associated with CO₂ capture and release. These studies would clarify physical and chemical changes associated with CO₂ capture by amidine containing copolymers.

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VITA

Danielle J. Chun was born in Pleasanton, California on June 11th, 1995. She graduated from California High School in 2013 and, that same year, went on to attend California Polytechnic (Cal Poly) State University at San Luis Obispo. While at Cal Poly, Danielle participated in two summers of undergraduate research in polymer chemistry under the mentorship of Dr. Shanju Zhang, and a year of academic research in Analytical Chemistry under the mentorship of Dr. Corinne Lehr. She also joined in several programs, including the Boys and Girls Club, to educate children about opportunities in the STEM fields. In 2017, Danielle received the Analytical Chemistry Research Award and graduated with her Bachelor of Science in Biochemistry. She then started her first industry position as a Chemist-I in the Clinical Diagnostics Division at Bio-Rad Laboratories in Hercules, California. In 2018, Danielle ventured to the University of Tennessee at Knoxville (UTK) to pursue a Doctor of Philosophy in polymer chemistry under the advisership of Professor S. Michael Kilbey II. Her research focuses on the study of the physical and chemical behaviors of amidine-functionalized polymers in response to the capture and release of carbon dioxide. During her tenure at UTK, she assumed a leadership position in the Multicultural Graduate Student Organization (MGSO), recognized with the "Graduate Organization of the Year" award consecutively for the academic years 2022-2023 and 2023-2024.