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I am submitting herewith a dissertation written by Christopher Michael Bottoms entitled “Accelerated Catalyst Diffusion in Chemically Amplified Resists.” I have examined the final paper copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemical Engineering.

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Accelerated Catalyst Diffusion in Chemically Amplified Resists

A Dissertation Presented for the
Doctor of Philosophy
Degree

The University of Tennessee, Knoxville

Christopher Michael Bottoms

May 2022

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*Dedicated to, and in memory of, Billy Dean Gentry. Not a day goes by that I do not miss
your affection, encouragement, and pride for my accomplishments.*

Acknowledgments

Throughout my graduate studies I have received tremendous support:

I would first like to express my heartfelt gratitude to my advisors Dr. Gila Stein and Dr. Manolis Doxastakis. Without their skillful guidance, endless support, constructive critique, and continued willingness to make the time to “meet real quick”, even on their busiest days. Without their mentorship this dissertation would never have been possible and I can never fully express the sincere appreciation I have for the two of them.

I would also like to thank my dissertation committee members: Dr. Bamin Khomami, Dr. Stephen Paddison, and Dr. Ioannis Sgouralis. Their willing support and feedback on my dissertation studies has been instrumental in the improvement of my research and has assisted me in reaching this hard-earned milestone.

My research would not have been possible without our close collaborator Dr. Tanguy Terlier at the Shared Equipment Authority at Rice University. I would like to extend my sincere gratitude to him. In addition I would like to thank the Polymer Characterization Lab at the Joint Institute for Advanced Materials for continued access to their instrumentation.

I express thanks to the National Science Foundation for grants CBET-1731185 and CMMI-1727517, as well as the University of Tennessee, for providing the financial support necessary for the completion of my studies.

I am incredibly grateful for my group members, in both Dr. Stein and Dr. Doxastakis’ research groups, especially Jonathan Coote, Travis Laws, Nobahar Shahidi, and Karthika Madathil for being there for me since (or almost since) the beginning. The conversations,

meals, friendship, assistance, and laughs we share with each other every day will be sorely missed. I give a special thanks to our former undergraduate researcher Grant Bauman, who worked with me on perfecting the reaction kinetics analyses, we've missed you.

I would like to thank every one of my friends and colleagues, those who I have bonded with at the university, through music, and in life, of which there are too many to name. In particular, I would like to thank Dr. Gaurav Chauhan for his constant enthusiasm to go to lunch and converse about life, diffusion models, and the music of The Beatles.

Last but certainly not least, I express my deepest gratitude to my family (those with us and those not) for their love, support, and standing by me every day of my life. I owe my love for life and learning to their encouragement. This especially includes my fiancé, Jessica Habel, and my soon-to-be family that accepted and supported me from the day we met.

GROMACS reminds you:

“They’ve done studies, you know. 60% of the time, it works every time.” (Brian Fantana)

Abstract

Quantitative reaction-diffusion models are critical for the development of high-resolution lithographic processes based on chemically amplified resists (CARs). CARs consist of a glassy polymer resin with a photoacid generator. Patterns are formed through a coupled reaction-diffusion process. It is known that reaction kinetics is controlled by the slow diffusion of acid-anion pairs (catalysts), and catalyst diffusion lengths partly control the pattern resolution and uniformity. However, it is difficult to quantify the diffusivity during reaction, let alone examine the roles of polymer-ion and ion-ion interactions on catalyst mobility, using direct measurements. This work presents a concerted experimental and computational effort to probe catalyst diffusion in a model CAR. Depth profiling experiments using time-of-flight secondary ion mass spectrometry offered a direct measure of catalyst diffusion lengths at moderate temperatures, while reaction kinetics was monitored with in-situ Fourier transform infrared spectroscopy. Multi-microsecond molecular dynamics simulations provided insight into ion-ion association, polymer-ion interactions, and transport mechanisms that influence diffusivities at temperatures well above the glass transition. By studying both reactive and inert CARs, it was shown that catalyst diffusion is significantly accelerated by reaction. It was hypothesized that this acceleration stems from plasticization by photoactivation and/or reaction byproducts, the generation of excess free volume following reaction, or a combination of these effects. Experiments confirmed that byproducts were present in the film and could contribute to accelerated catalyst diffusion, but this alone could not account for the discrepancy between reactive and inert CARs. Simulations showed that generation of excess free volume transiently accelerates local catalyst diffusivities, and that clustering

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Chapter 1

Introduction

Moore’s law, or the predicted doubling of the number of transistors in an integrated circuit every 18 months, has pushed the development of new transistor patterning technologies for decades. However, many experts are predicting the break down of this long-held trend, in part due to transistor patterning dimensions approaching molecular length scales.[1] Photolithography, which creates patterned masks in a photosensitive film (“photoresist”) for selective etching or deposition of materials, continues to be the dominant technology for transistor patterning

Photolithography relies on a thin film photoresist that changes its solubility upon exposure to UV light. The patterns are developed by immersion in a solvent that selectively dissolves either the reacted or unreacted areas. The forefront technology for sub-7 nm node patterning is known as extreme ultraviolet (EUV) lithography.[2] Resists that are exceptionally sensitive to low doses of EUV radiation are required to perform high-throughput EUV lithography, and this requirement is met with a class of resists known as chemically amplified resists (CARs).[3,4]

Polymeric CARs contain a glassy polymer resin with acid-labile protecting groups paired with a photoacid generator (PAG). When irradiated by deep ultraviolet (DUV) or EUV light, the PAGs decompose to produce acid-anion pairs (catalysts). When subsequently heated at moderate temperatures the ion pairs diffuse, catalyze the scission of nearby protecting groups,

and regenerate to allow for further catalysis events.[5,6,7] These processes are illustrated in Figure 1.1. The “deprotection” reactions are typically designed to increase the polymer’s polarity so the patterns can be developed. Since reaction is coupled to catalyst diffusion, there is a trade-off between the need for diffusion to drive reaction events, and the need to limit “blur” and “roughness” of the patterns due to diffusion outside the exposed regions.[2,8] However, the complex interplay between the reacting polymer matrix and the diffusion of the catalyst is not well understood, which makes it difficult to predict and control catalyst diffusion and the spatial extent of deprotection.

In most CAR materials, the reaction produces polar moieties that can strongly interact with each other, with other polar groups on the polymer, and with the diffusing acid-anion pair. As an example, APEX is a commercial CAR resin that was used for DUV lithography in the 1990s, and is based on poly(4-*tert*-butoxycarbonyloxystyrene) (PtBOCSt) which is deprotected to poly(4-hydroxystyrene) (PHOSt). Later DUV resins were based on terpolymers of HOSt, styrene (St), and *tert*-butyl acrylate (tBA), where the deprotection of tBA produces acrylic acid (AA). A common feature of HOSt-based resists is that the diffusion of the acid-anion catalyst is much slower than the local deprotection reaction at typical reaction temperatures, so the reaction is controlled by catalyst diffusion.[9] However, it is difficult to quantify catalyst diffusivities through direct measurements, especially at nanometer length scales, and even more challenging to examine the role of polymer-ion and ion-ion interactions and polymer densification on catalyst mobility.

Models informed by experimental data can provide predictions for fine-tuning the process conditions prior to experimental investigation. As a result, many efforts have focused on building a mathematical framework for the reaction-diffusion process in CARs. It was recognized early on that a model of Fickian diffusion coupled to instantaneous local reaction does not quantitatively capture experimental data,[10] so additional phenomenological processes were incorporated to improve the description. These processes were designed to approximate changes in reaction rates due to proposed acid-polymer or acid-acid interactions, typically through the incorporation of a reduction in the concentration of the catalyst or through polymer composition-dependent diffusivities. Such models had limited success in

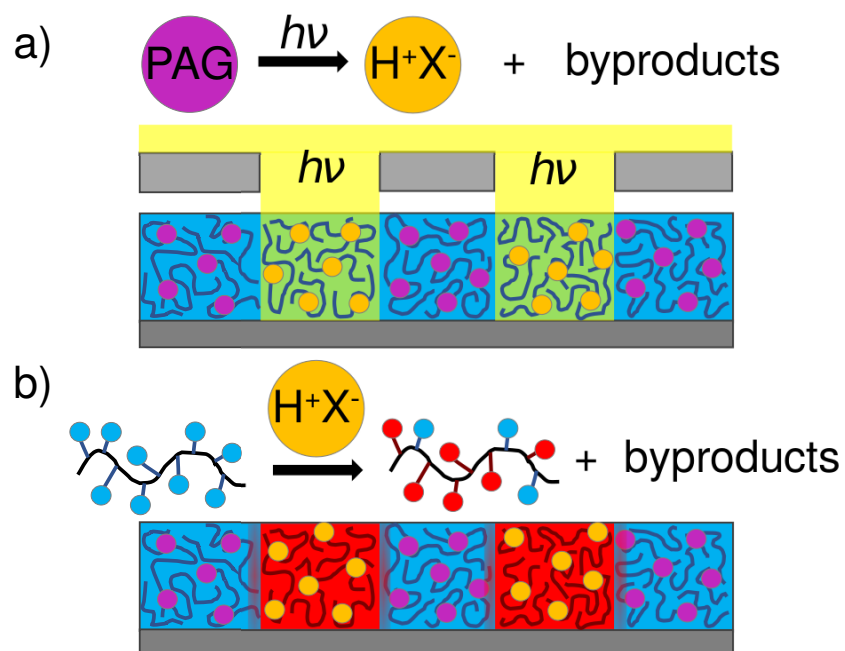


Figure 1.1: Schematic of CAR patterning. a) Light-induced activation of PAGs produces the acid-anion catalyst and byproducts. b) Heating at moderate temperature activates the acid-catalyzed deprotection reaction. Protected and deprotected sites are illustrated in blue and red, respectively.

describing reaction kinetics, however the lack of experimental data to verify such processes prevented further refinement.

The CAR system that was used to inform many of these early developments was a blend of PtBOCSt, a PAG, and in some cases a base additive. The acid-catalyzed deprotection of PtBOCSt produces PHOSt with volatile byproducts (carbon dioxide, 2-methylpropene).[3] Ferguson and co-workers reported that the PtBOCSt deprotection rate follows a power law dependence on acid concentration and does not reach complete conversion, indicating that an acid loss mechanism might be warranted.[11] Acid loss is often described as a “trapping” process that is attributed to strong local interactions with the polymer (such as hydrogen-bonding) or neutralization due to contaminants, and is observed in a variety of CAR chemistries.[12, 13, 14] The acid loss or “trapping” process has been modeled by either a first-order or second-order reaction.[8, 9, 15]

Studies have also suggested that employing Fick’s law with a constant diffusion coefficient is inadequate, and either a linear combination of two diffusion coefficients or models that produce local acceleration due to a short-lived increase in free volume upon reaction should be used instead.[7, 10, 15, 16, 17, 18] Following the latter approach, Croffie and co-workers developed a model with a set of six differential equations which, after some simplifications, invoked six parameters to qualitatively describe the spatial extent of deprotection in PtBOCSt patterning.[19] However, Hinsberg later argued against the concepts of plasticization and free volume accumulation by showing that PtBOCSt deprotection is much slower than byproduct volatilization.[20] Therefore, in order to construct a predictive model for the reaction-diffusion processes in CARs, it is evident that we must identify the dominant fundamental mechanisms and then determine the minimal set of necessary parameters.

A central component in the development of a model of the reaction-diffusion process is determining catalyst diffusivities in the reactant and product, as well as any local acceleration/deceleration due to reactions and/or interactions with specific chemical groups. Hinsberg, Houle, and co-workers modeled the coupled reaction-diffusion process in PtBOCSt

using Fick’s law with a composition-dependent diffusivity.[21, 22] They reported that acid diffusion is controlled by counter-anion size, and that acid diffusivity is 1-2 orders of magnitude higher, with a larger activation energy, in the non-polar reactant than in the polar product. Therefore, differences between the two diffusion rates are reduced as temperature is decreased. Ober, Thompson and coworkers measured reaction kinetics and catalyst diffusivities during reaction as a function of polymer chemistry and catalyst size in a variety of resist chemistries, including PtBOCSt, at temperatures far above glass transition (> 500 K) using laser-induced submillisecond heating.[23, 24] They record fast first-order reaction kinetics at these high temperatures and highlight the importance of combining fast reaction rates with slow diffusion rates to optimize patterning performance. They also found that acid diffusion rates are slowed with increased anion size and increased film density. Willson and coworkers measured approximate diffusion lengths in nonreactive analogues of PtBOCSt at temperatures near the glass transition and then estimated the diffusivities using Fick’s law.[25] They noted that these estimates were not large enough to account for the observed short-time diffusion rates during PtBOCSt deprotection,[17] offering support for models where reaction locally enhances the diffusivity. These authors also examined PtBOCSt deprotection kinetics with an anion-bound polymeric PAG, and showed that mobility of the proton is highly coupled to that of the anion.

One of the challenges with determining the composition-dependent catalyst diffusivity is that few experimental techniques can directly resolve the shape of the diffusion front. Instead, many early works used infrared absorbance spectroscopy to monitor bulk deprotection kinetics in PtBOCSt.[21, 22] Samples were prepared with an acid catalyst gradient and diffusivities were estimated through analysis of experimental data with proposed reaction-diffusion models. Other studies employed model trilayer experiments where the polymer of interest (*i.e.*, an inert PtBOCSt analogue or PHOST) was sandwiched between an acid feeder layer and a detector layer. The diffusivity in the polymer of interest was estimated by Fick’s law using the acid transit time through the middle layer of known thickness.[17, 25] A later study examined the shape of the reaction front with neutron reflectivity (NR).[26] An acid feeder layer was placed on top of partially-deuterated PtBOCSt, and samples were annealed

for a specified time at fixed temperature. NR was then used to determine the spatial extent-of-deprotection from changes in scattering length density due to volatilization of protecting groups. This approach for resolving the spatial deprotection profile has since been extended to other CAR systems, including candidate chemistries for EUV lithography.[27,28,29] These data can be reproduced by a reaction model based on two differential equations, one for deprotection and another for Fickian acid diffusion with added “trapping”, [8, 27] thereby avoiding the challenge of independently determining the large number of physical parameters in more complex models. However, this analysis relies on the applicability of Fick’s second law and the phenomenological acid trapping process.

Diffusion of small inert penetrants in polymer melts and glasses has been studied by molecular models for more than two decades.[30, 31, 32, 33] Given the complexity of CAR systems, early models did not include molecular detail aside from a few examples that resorted to significant simplifications.[34, 35] However, with the rapid increase in computational power, ionic diffusion in inert polymers[36, 37, 38, 39, 40] and in CAR systems[41, 42, 43] is now studied with models that aim to incorporate atomistic detail. Recently, Kim and co-workers presented a multiscale study that combined density functional theory (DFT), molecular dynamics (MD) simulations, and finite differences method (FDM) to explore photoacid dissociation, polymer deprotection, and solubility switching of individual macromolecules.[42] The chemistry examined was PHOST that was partially protected by *tert*-butoxycarbonyl groups, *i.e.* a copolymer of HOST and tBOCSt. The main aim of their work was to examine CAR materials at a sub-10 nm scale beyond the homogeneous volume element description of mesoscopic models. The dissociation reaction of PAGs was treated based on DFT-derived data while molecular dynamics implemented the PCFF atomistic forcefield for acid-acid and acid-polymer interactions. The authors observed agglomeration of photoacids at high PAG loadings, but the investigation of such acid-acid interactions within the polymer matrix was limited by the relative short MD simulation employed (total of 3 nanoseconds). The positions of the reactive protecting groups and the acid molecules were mapped to a continuum FDM model that was used to examine the coupled reaction-diffusion mechanisms. The authors used a deprotection rate constant determined

by their DFT analysis, and a diffusivity, D , of 5.6×10^{-14} cm²/s that was estimated in an early literature study by fitting experimental data of bulk deprotection kinetics with a mesoscopic reaction-diffusion model.[10] In a subsequent study, Kim and coworkers reported stochastic simulations that incorporated details of the dynamics that were probed by MD. Specifically, by identifying accessible sites in the reactant polymer via free volume analysis and tracking hopping events during short MD simulations, the authors estimated a D value of $2.5 - 2.9 \times 10^{-14}$ cm²/s. A kinetic Monte Carlo mesoscopic simulation was designed with the addition of a localized trapping event when the diffusing acid is in proximity to the reactive protecting group.[43] It remains to be seen if such multiscale methods can quantitatively capture the recorded deprotection kinetics in CAR systems and contribute to materials discovery for the next generation of CAR materials.

1.1 Research goals

My research is centered on the characterization of the physical processes that control catalyst diffusion during reaction, and the development of mesoscopic models of CAR reaction kinetics that are informed by these processes. Prior studies show that, in HOS_t-based CARs, catalyst diffusivities are significantly enhanced by the reaction.[10, 17, 19, 25] The goal of this dissertation is to identify the chemical and physical origins of accelerated catalyst diffusion. The approach is based on a concerted experimental and computational effort that probes a broad range of length- and time-scales. Efforts have consisted of six main thrusts: In Chapter 2, we performed experiments to measure reaction kinetics of a CAR system consisting of triphenylsulfonium triflate, (TPS-TFL), photoacid generator and the terpolymer resist poly(4-hydroxystyrene-*co-tert*-butyl acrylate-*co*-styrene), P(HOS_t-tBA-St). The results of these experiments were compared to literature models of diffusion-controlled reaction to test the assumptions of these models. In Chapter 3, in an effort to understand the factors that control catalyst diffusion and account for failings of the literature models, we examined diffusion in the absence of reaction using an inert catalyst analogue. In Chapter 4, to determine the origin of experimentally observed accelerated

catalyst diffusion during reaction, we performed atomistic simulations of protecting group removal to interrogate the physical processes behind accelerated catalyst diffusion at the molecular level. In Chapter 5, we developed a physics-informed 3-dimensional lattice model of reaction due to transient local catalyst diffusion states that captures reaction kinetics observed both in simulations at high temperatures and in experiments below glass transition. In Chapter 6, we employed the model to gather information on experimentally inaccessible metrics of the CAR systems: the impacts of catalyst counter-anion size on catalyst clustering and the predicted generation and relaxation of excess free volume. In Chapter 7, we measured catalyst diffusion and deprotection fronts using time-of-flight secondary ion mass spectrometry to further our understanding of the interplay between the spatial extent of catalyst diffusion and reaction which will, in on-going work, be compared to the physics-informed model of catalyst diffusion. The results of this effort are an important step in understanding the controlling factors of catalyst diffusion in CARs, which will guide the development of predictive models of reaction and catalyst diffusion in CAR systems for the further development of lithographic processes.

Chapter 2

Reaction kinetics in CARs

This section describes an improved method of measuring reaction kinetics using infrared spectroscopy for our model CAR system and the comparison of reaction kinetics to literature models of reaction induced by catalyst diffusion. The affects of catalyst concentration and temperature on reaction kinetics are examined. The assumptions of literature models are examined to help guide the development of physics-informed models of reaction kinetics described in later chapters.

2.1 Methods

2.1.1 Materials

Polymers. The protected polymer used for our studies is poly(4-hydroxystyrene-*co*-*tert*-butyl acrylate-*co*-styrene), referred to interchangeably as the “protected polymer” or P(HOSt-tBA-St), and was provided by DuPont Electronic Materials. P(HOSt-tBA-St) is deprotected to poly(4-hydroxystyrene-*co*-acrylic acid-*co*-styrene), referred to interchangeably as the “deprotected polymer” or P(HOSt-AA-St). Model trimers of each chemistry are

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depicted in Figure 3.1. The weight-average molecular weight and dispersity were 7.0 kg/mol and 1.6, respectively, as determined by gel permeation chromatography (GPC) based on a polystyrene calibration. The molar composition was 55% HOS_t, 25% tBA, and 20% St, as determined by hydrogen nuclear magnetic resonance spectroscopy (¹H-NMR). The chemical deprotection of P(HOS_t-tBA-St) to produce P(HOS_t-AA-St) was performed following procedures reported in the literature.[44] P(HOS_t-tBA-St) was dissolved in 1,4-dioxane (>99% pure, Fisher Scientific) with a mass ratio of 50:1 solvent to polymer. Hydrochloric acid (HCl) (37 wt%, Fisher Scientific) was added at a mass ratio of 10:1 solvent to acid, and the mixture was refluxed at 383 K for 24 h. Purification and precipitation of the P(HOS_t-AA-St) product entailed: removing 1,4-dioxane and remaining HCl with a rotavap at 348 K; dissolving in tetrahydrofuran (THF) (>99.9% pure, Fisher Scientific); precipitating into roughly 273 K hexanes (>98.5% pure, Fisher Scientific); gravity filtration using Whatman™ grade 41 filter paper; and drying under vacuum at 333 K for 8 h. This process was repeated twice to remove HCl and other contaminants in the polymer. The final product was dried under vacuum at 383 K for 24 h to remove residual 1,4-dioxane from the polymer.

Catalyst. Triphenylsulfonium triflate (TPS-TFL) was obtained from Sigma-Aldrich. Triphenylsulfonium triflate was used to generate acid triflate (H⁺TFL⁻) with near-100% efficiency by exposing films to deep ultraviolet light (254 nm) at a dose of 135 mJ/cm². [45] The photodecomposition of TPS-TFL produces a variety of catalyst activation byproducts, as shown in Figure 2.1. A few of these byproducts are expected to be non-volatile remain within the films. At moderately elevated temperatures, the catalyst promotes the scission of tBA groups which produces AA groups, produces small molecule volatile byproducts (the most prominent being 2-methylpropene), and regenerates the catalyst for further reactions, Figure 2.2.

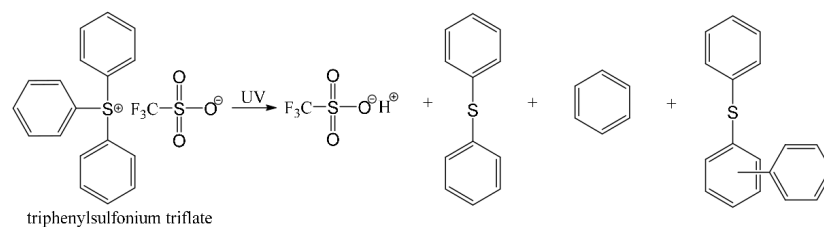


Figure 2.1: Decomposition of photoacid generator upon exposure to UV light.

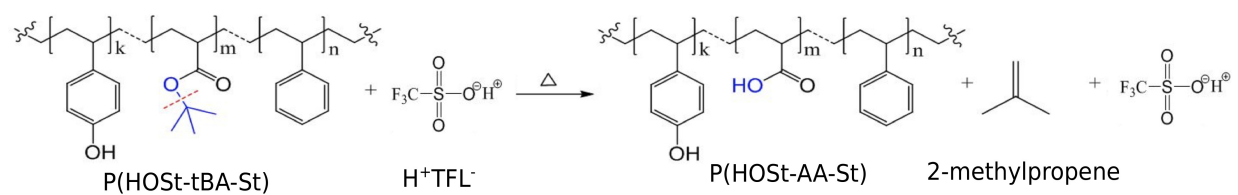


Figure 2.2: Deprotection reaction of model photoresist polymer.

2.1.2 Experiments

Deprotection Reaction. Solutions containing 8 wt% P(HOSt-tBA-St) in PGMEA and 0.24, 0.40, and 0.56 wt% TPS-TFL (3, 5, and 7 wt% TPS-TFL with respect to the polymer) were spin-coated onto silicon wafers at 2000 rpm. The films were baked at 403 K for 4 mins to remove residual PGMEA. This produces P(HOSt-tBA-St) films with 0.05, 0.08, and 0.11 μm^3 TPS-TFL at a thickness of approximately 250 nm. The TPS-TFL was activated following the previously-described procedure. The reaction progress was monitored with in-situ Fourier Transform Infrared (FTIR) Spectroscopy (Nicolet) at temperatures of 335, 340, 345, and 350 K. by tracking the absorbance of the C-O stretch of tBA at 1148 cm^{-1} .^[45] After loading of the sample, the apparatus returns to the target temperature of 350 K within 20 s. A reference sample of the fully deprotected polymer, P(HOSt-AA-St), was prepared and measured via FTIR following the same method. The deprotection level of the P(HOSt-tBA-St) reactant was calculated by subtracting the P(HOSt-AA-St) signal from each spectrum, normalizing by the initial absorbance, A , at time $t = 0$, and then calculating the area of the tertbutyl-oxygen absorbance at each time. The deprotection level, or extent of reaction, is defined as:

$$\text{Deprotection level} = \frac{A(t = 0) - A(t)}{A(t = 0)} \quad (2.1)$$

2.2 Literature models of reaction kinetics

We measured reaction kinetics of TPS-TFL photoacid generator and P(HOSt-tBA-St) using infrared spectroscopy and compare with literature models. To validate models for the coupled reaction-diffusion process, it is important to consider both the effects of catalyst loading and reaction temperature and their effects on catalyst diffusion. We determined that reaction kinetics cannot be described by models displaying Fickian diffusion of the catalyst, however models of subdiffusion of the catalyst more accurately described experimental data. We also find that literature models cannot describe the limited conversion at long-times shown in

reaction kinetics data across varying catalyst concentration, suggesting that more knowledge is needed about the origin of this limiting behavior.

Figure 2.3 shows FTIR data for a postbake temperature of 350 K with an acid catalyst loading of $0.11 \text{ \#}/\text{nm}^3$. Figure 2.3 also reports the experimental deprotection kinetics of P(HOSt-tBA-St) at 350 K with $0.11 \text{ \#}/\text{nm}^3 \text{ H}^+\text{TFL}^-$ and a comparison with three literature mesoscopic models.[13, 17, 27, 45, 46, 47] The first is a simple description coupling Fickian catalyst transport with a fast pseudo-first-order deprotection reaction (Figure 2.3a).[13] The Fickian diffusivity, D , that controls transport in a lattice-based Kinetic Monte Carlo (KMC) algorithm is an adjustable parameter for optimization and catalysts are distributed randomly to maintain the known bulk concentration. This algorithm is based on Gillespie’s stochastic method for translational dynamics. The deprotection reaction occurs instantaneously when cells of 1 nm^3 size are visited by the catalyst, since local reaction is known to be much faster than catalyst diffusion at these temperatures.[22] The optimized value of D for these conditions is $2 \times 10^{-16} \text{ cm}^2/\text{s}$, similar to other models of CAR reaction kinetics.[10, 42, 43] The model does not provide a quantitative description of the temporal evolution of deprotection level, however it does provide a rough estimate of the average catalyst dynamics during reaction. Specifically, this model slightly underestimates the deprotection level at short times and greatly overestimates it at long times as the model predicts complete deprotection.

The limited conversion of the material at long times is often captured with a phenomenological catalyst trapping process,[13, 15, 27, 28] such as the second-order model $d[\text{H}^+]/dt = -k_t\phi[\text{H}^+]$, where ϕ is the deprotection level and k_t is the trapping parameter (Figure 2.3b). These studies rationalize this process as a product of strong interactions between the catalyst and deprotected sites along the polymer chain which could limit catalyst transport.[8, 13] This model predicts the same diffusivity of $D = 2 \times 10^{-16} \text{ cm}^2/\text{s}$ with a value of $k_t = 6 \times 10^{-4} \text{ s}^{-1}$. Figure 2.4 provides model parameters as a function of temperature and photoacid size, that are fit simultaneously to all datasets for all concentrations at the respective temperature. Diffusivities, predictably, decrease as a function of temperature, however little change is observed in the trapping parameter.

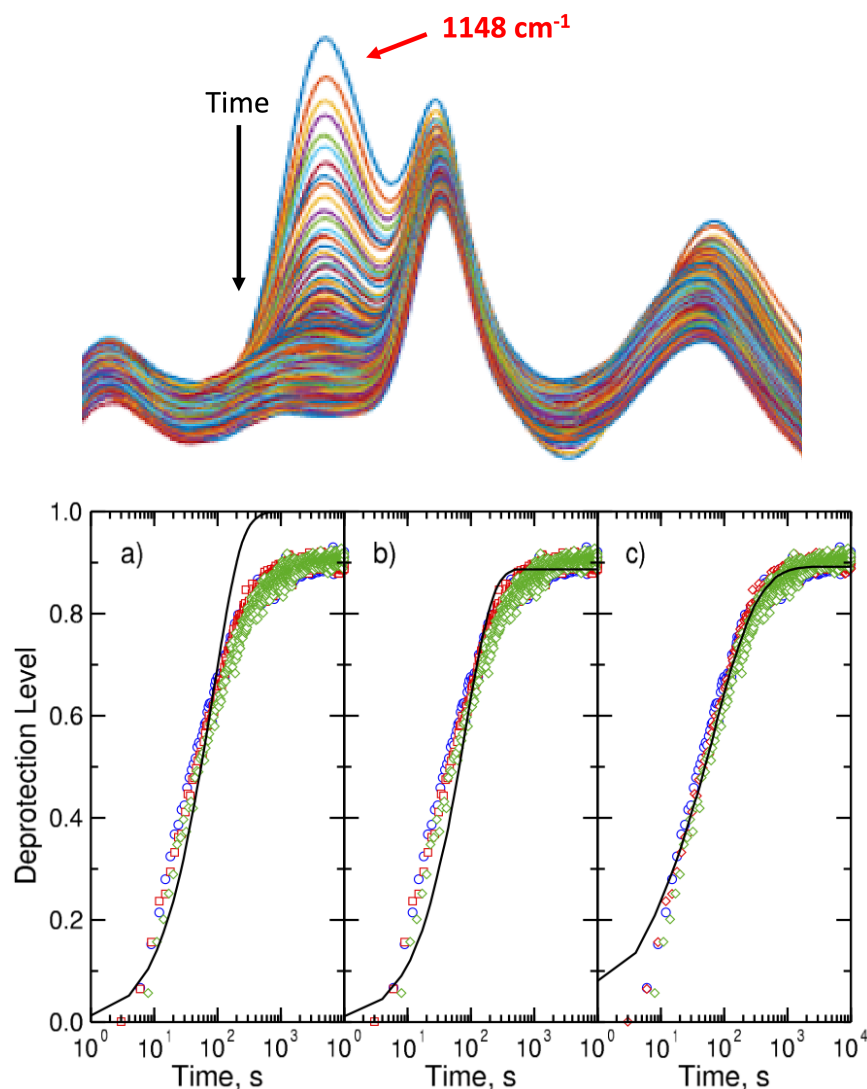


Figure 2.3: (Top) Time resolved FTIR data of absorbance vs. wavenumber, the 1148 cm^{-1} peak corresponding to reaction progression decreases over time. (Bottom) Stochastic models of diffusion-controlled deprotection kinetics in CARs (solid black lines) compared with experimental data (symbols) for P(HOSt-tBA-St) with $0.11\text{ \#}/\text{nm}^3$ of H^+TFL^- at 350 K. Different symbols correspond to independent measurements. a) KMC with Fickian diffusion; b) KMC with catalyst trapping coupled to Fickian diffusion; and c) Monte Carlo simulation with subdiffusive catalyst transport and catalyst deactivation. The local reaction occurs instantaneously in all models.

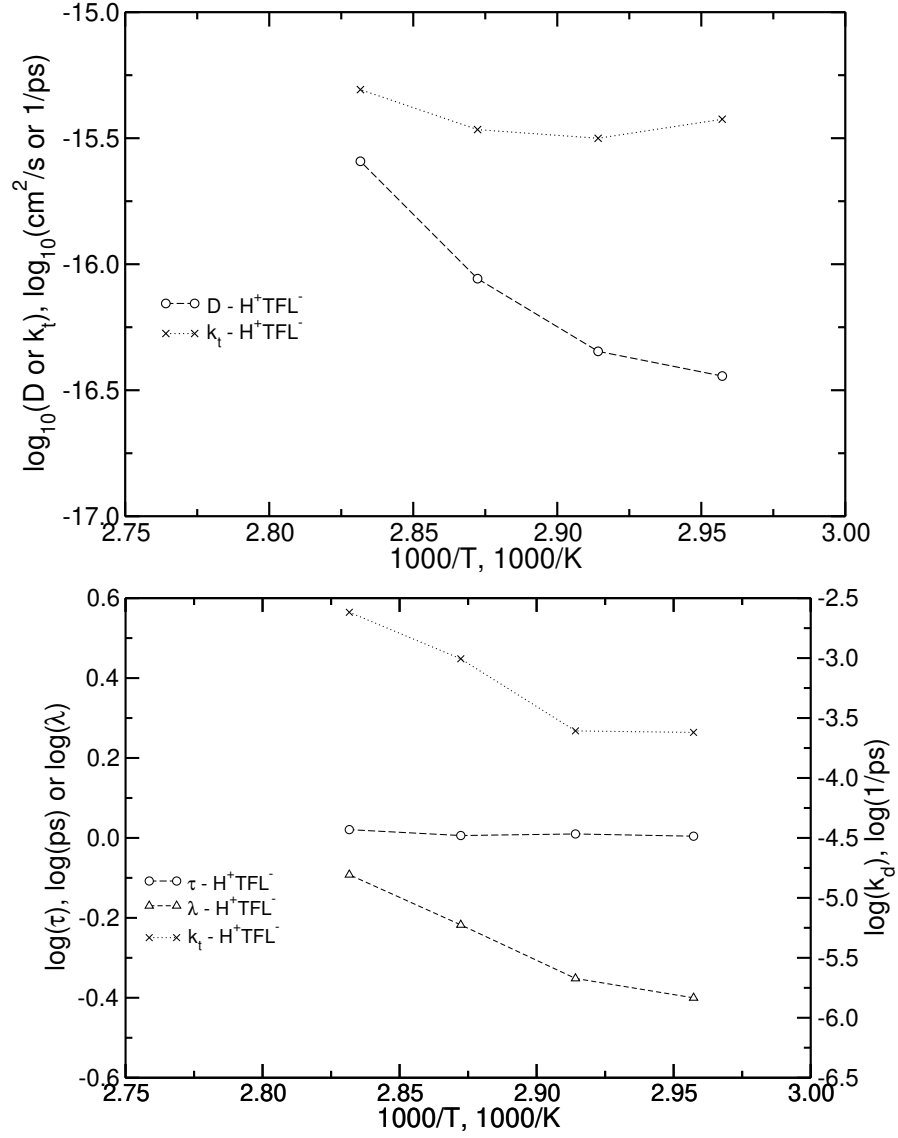


Figure 2.4: (Top) KMC with catalyst trapping coupled to Fickian diffusion parameters as a function of temperature for H^+TFL^- . (Bottom) Monte Carlo simulation with subdiffusive catalyst transport and catalyst deactivation parameters as a function of temperature for H^+TFL^- .

In past work from the Doxastakis and Stein groups, it was shown that reaction kinetics are quantitatively captured using mesoscopic models with subdiffusive transport, i.e. a time-dependent diffusivity (Figure 2.3c).[45] (Deviations at times less than 20 s are associated with transient heating.) Such behavior is often reported for penetrants in glassy polymers at nanometer length scales, and could be attributed to the effect of enthalpic interactions between the penetrant and polymer or to the movement of penetrants through transient volume between polymer chains[31]. A phenomenological process of linear catalyst deactivation was used to capture long-time behavior and follows the form $d[H^+]/dt = -k_d[H^+]$, [15] introduced post-calculation of waiting times in the continuous-time random walk formulation. The optimized parameters for 350 K and 0.11 #/nm³ H⁺TFL⁻ are $\tau = 1.3$ s, $\gamma = 0.78$, and $k_d = 3 \times 10^{-3} \text{ s}^{-1}$. Importantly, γ is a measure of the deviation from Fickian transport with values less than 1 indicating subdiffusive transport. Figure 2.4 also provides the parameters of this model as a function of temperature, that are fit simultaneously to all datasets for all concentrations at the respective temperature. It is observed that as temperature is decreased, diffusion becomes more subdiffusive. However, it is difficult to draw conclusions from the trends of k_d .

Commonly, across both the acid trapping and acid deactivation models, the limited conversion at long-times is only captured accurately when fitting at a single catalyst concentration which suggests a concentration dependence trapping/deactivation parameter that is not accounted for in either model. However, microscopic insight into the mechanisms responsible for such findings would help to determine the origins of these observations. Therefore, we performed detailed atomistic simulations coupled with experimental investigation to gain insight into the contributions of ion-ion and ion-polymer interactions to transport processes in a nonreactive model system, detailed in the following chapter.

2.3 Conclusions

Literature models of CAR reaction kinetics were compared to measured reaction kinetics to study their applicability to the reaction induced by the diffusion of H⁺TFL⁻ in the

protected polymer. Models that assume a constant catalyst diffusivity cannot describe the observed reaction kinetics, however models that display a subdiffusive nature of the catalyst (decreasing diffusivity over time) capture the shape of reaction kinetics. Models that demonstrate a catalyst trapping process or a catalyst loss process can capture the long-time scaling of reaction kinetics at a single catalyst concentration, however these processes do not capture the observed catalyst concentration scaling of reaction kinetics. These results suggested that catalyst diffusion is transient during reaction and that further investigation was necessary to discover the origin of the long-time scaling of reaction kinetics.

Chapter 3

Ion Diffusion in CARs

Herein, we present a concerted molecular simulation and experimental approach to study ion transport in the protected and deprotected forms of a model CAR terpolymer in which we eliminate the complications of a reactive system by replacing the acid-anion catalyst with an inert analogue. To examine the ion pair dynamics at high temperatures, we employ multi-microsecond MD simulations that reach the long-time Fickian diffusion regime so that we can directly extract the ion diffusivity in the two different polymers at various concentrations. To address the ion pair dynamics in the glassy state as a function of ion concentration and temperature, we undertake experimental investigations using time-of-flight secondary ion mass spectrometry (TOF-SIMS). TOF-SIMS is a technique for chemical analysis that provides real-space depth profiles in organic and inorganic materials,[48] including polymer blends,[49, 50, 51, 52] polymer-based composites,[52, 53, 54] and block copolymers,[52, 55] yet it is rarely exploited to examine acid diffusion in CARs.[56, 57] Our results demonstrate that long-range transport in these materials is much slower than predicted by reaction-diffusion models of CAR materials. In addition, we show that ion-ion interactions are present in CARs but have minimal impact on transport in the absence of reaction.

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3.1 Methods

3.1.1 Materials

Polymers. The protected polymer, P(HOSt-tBA-St), was obtained from Dupont Electronic Materials and the deprotected polymer, P(HOSt-AA-St), was obtained through chemical deprotection of the protected polymer.[44]. Further information is provided in Chapter 2. The glass transition temperatures of P(HOSt-tBA-St) and P(HOSt-AA-St) were measured through spectroscopic ellipsometry (described later). Appendix A includes a complete description of GPC and ^1H -NMR instrumentation, as well as the related data and analyses (Figure A.1 and A.2).

Ionic Penetrants. Sodium triflate (Na^+TFL^- , >98% pure) was obtained from Sigma-Aldrich and stored under inert gas to prevent degradation.

3.1.2 Simulations

Models and Forcefields. The forcefield parameters for the ions, the sodium cation (Na^+) and the triflate counter-anion (TFL^-), were adopted from Zhong et al.[58] and follow a united-atom approach where fluorine atoms are lumped together with directly connected carbon atoms into a single interaction site (Figure 3.1). As is typical in simulations of ionic liquids, the magnitude of the charges of the ions are reduced to 0.8e to better capture dynamics in the absence of induced polarization.[59,60] We note that in a preliminary effort with an explicit-atom model for the triflate counter-anion and full charges[61] extensive ion-ion interactions and complete aggregation/phase-separation of the ions within our polymer models was found. While some association is expected, which is further discussed in Section 3.2.3, complete phase separation is not supported by experimental data of these materials. In contrast, the combination of the united-atom ion model used herein with the polymer forcefield delineated below (and described in further detail in Appendix A) appears to provide a realistic and efficient description of both thermodynamic and dynamic properties.

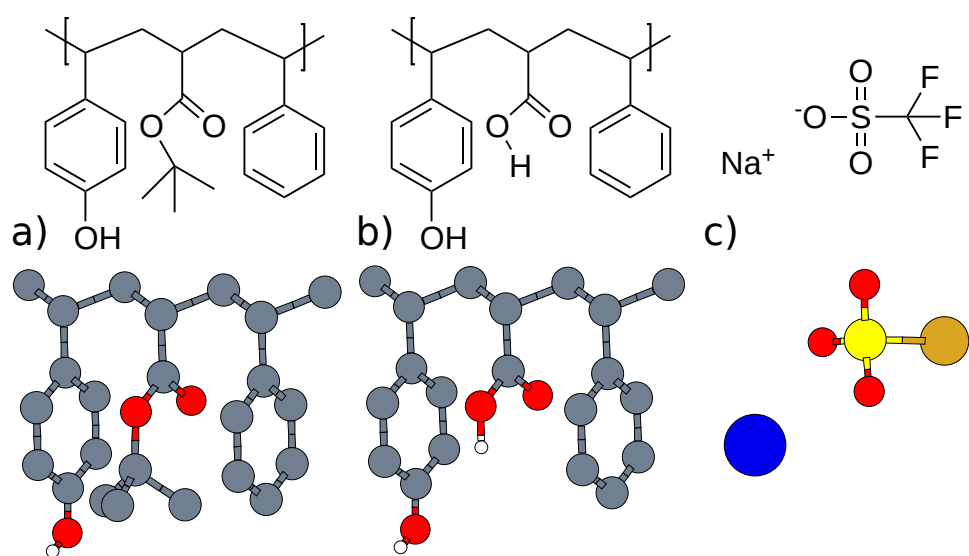


Figure 3.1: United-atom trimer models of a) P(HOSt-tBA-St); b) P(HOSt-AA-St); and c) Na⁺TFL⁻.

The TraPPE-United Atom forcefield was adopted for the terpolymers as described in the literature.[62, 63, 64, 65] Non-polar hydrogens and directly connected carbon atoms are lumped into a single “united atom” interaction site (Figure 3.1). The TraPPE forcefield has been parameterized based on extensive comparison to thermodynamics of small molecular compounds. Note that for phenols a recent explicit-atom description of the forcefield is preferred to more accurately capture quadrupole moments of these small ring molecules and their phase-equilibria.[66] However, we chose to adopt a united-atom model for our systems, keeping only the hydroxyl group in PHOST in an explicit representation as commonly performed for other alcohol systems modeled with TraPPE.[63] This simplification aims to increase performance, which is critical so that we follow the temporal evolution of our systems for sufficiently long trajectories. Furthermore, the forcefield parameters selected for this study accurately captured the elevation of the glass transition in P(HOST-AA-St) relative to P(HOST-tBA-St) terpolymers as recorded by spectroscopic ellipsometry (discussed further in Section 3.2.1).

The parameters for Lennard-Jones and Coulombic interactions as well as the intramolecular terms of the forcefield associated with bonds, angles, and dihedrals are summarized in Tables A.1, A.2, A.3, and A.4 in Appendix A. Lennard-Jones and Coulombic interactions between intramolecular neighbors are fully accounted for when separated by more than three bonds. Cross-interaction parameters (including ion-polymer pairs) were calculated based on the Lorentz-Berthelot rule as originally in TraPPE. 1-4 Coulombic interactions were included but scaled by 0.5.[67]

Software and Algorithms. Atomistic molecular dynamics simulations of P(HOST-tBA-St) and P(HOST-AA-St) with Na^+TFL^- ions were conducted using GROMACS 2018.1.[68] The leap-frog algorithm was used for integration.[69] Bond constraints were implemented using LINCS.[70] A cutoff of 1.4 nm was employed for Van der Waals interactions using a Verlet neighbor list. Short- and long-range electrostatics were accounted for with the smooth Particle-Mesh Ewald algorithm.[71] The temperature was maintained at desired values using the stochastic velocity rescale method.[72] Prior to long simulations in the

NVT ensemble, systems were brought to an equilibrium density using initial simulations with pressure coupling (and long-range dispersion corrections for energy and pressure) with the Berendsen algorithm.^[73]

Initialization. Polymer configurations consisting of 100 chains with 20 repeat units were constructed in a linear configuration using a statistical distribution of the respective monomers. Subsequent short simulations of approximately 15 ns at the elevated temperature of 570 K were employed to equilibrate the terpolymer systems. Minute cavities were then randomly introduced throughout the system with their radius progressively increased (with in-between steps of energy minimization) toward creating a spherical volume sufficient to accommodate a pair of Na^+TFL^- ions free of any steric overlaps. The number of these cavities (radii of approximately 0.4 nm) was set based on the desired ion concentrations at equilibrium density. Short NPT simulations (approximately 1 ns) at 570 K were sufficient to relax any free volume due to the cavities after insertion of the ions. Initial configurations of P(HOSt-tBA-St) and P(HOSt-AA-St) with ionic penetrant loadings of 0.05, 0.08, and 0.11 #/nm³, corresponding to 0.20, 0.34, and 0.48 ion-pairs/chain for P(HOSt-tBA-St) and 0.16, 0.27, and 0.40 ion-pairs/chain for P(HOSt-AA-St), respectively, were prepared with the above procedure at 570 K and then cooled to 520 K, 470 K, and below using a ramp of 10 K/ns in the NPT ensemble to a) obtain initial configurations for long NVT simulations; and b) examine the glass transition of the virtual material. Simulations of polymer and ion dynamics were performed in the NVT statistical ensemble at 570 K, 520 K, and 470 K with a time step of 1.5 fs for 1, 5, and 10 μs , respectively. Long trajectories were recorded at a pace of ~ 200 ns/day using the efficient models and software described herein along with Nvidia graphics processor units. This ensures that all memory from the initial configuration is lost and maximizes the sampling performed.

3.1.3 Experiments

Preparation of Bilayer Samples. Bilayer samples consisted of a base “feeder layer” and a top “diffusion layer” on silicon and were prepared as illustrated in Figure 3.2. The feeder

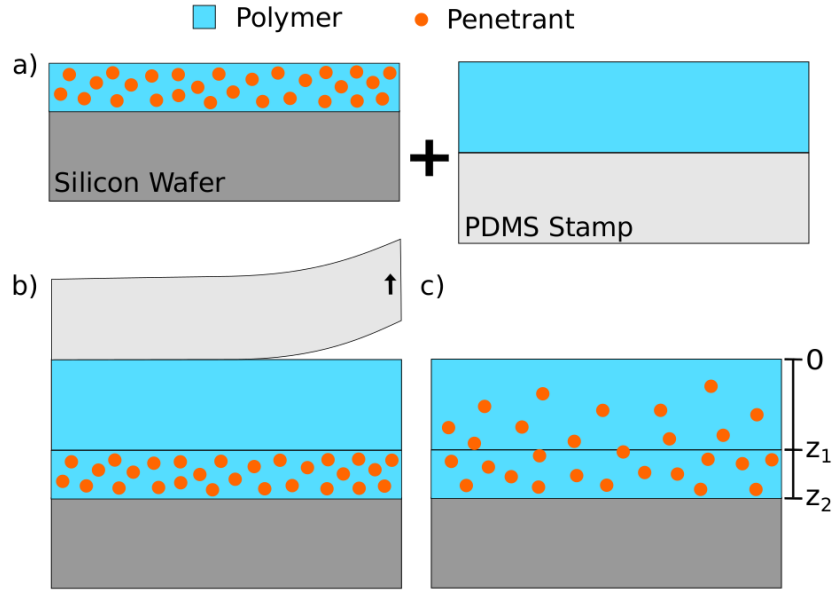


Figure 3.2: Preparation of bilayer samples TOF-SIMS experiments to probe ion diffusion. a) Polymer film on silicon with ionic penetrant (small circles) and polymer film on PDMS stamp without ionic penetrant. b) A pure polymer film is stamped onto a silicon-supported polymer layer with ionic penetrant, creating a bilayer with a well-defined interface. c) Schematic of ion distribution after heating at elevated temperature.

layer was a blend of polymer and ionic penetrant, and the diffusion layer was the same polymer without ionic penetrant. The polymer was either P(HOSt-tBA-St) or P(HOSt-AA-St). The diffusion layer was transferred on top of the feeder layer by stamping with a polydimethylsiloxane (PDMS) stamp that was prepared from a Dow SYLGARD™ 184 PDMS kit. A 1:7 (wt:wt) blend of hardener and base PDMS were poured onto a silicon wafer that was coated with n-octadecyltrimethoxysilane (Gelest, Inc.) and annealed under low vacuum at 353 K overnight. The crosslinked PDMS was then carefully peeled from the wafer, producing an elastomeric stamp with a smooth surface.

First, the feeder layer was prepared by spin-casting the polymer/penetrant blend from propylene glycol monomethyl ether acetate (PGMEA, >98% pure, TCI Chemicals) onto a clean silicon wafer (Figure 3.2a). The polymer loading in PGMEA was approximately 8 wt% in solution, and the Na^+TFL^- concentration was 0.05, 0.08, or 0.11 $\#/\text{nm}^3$ in the resultant film. Na^+TFL^- concentrations were calculated based on an estimated polymer density of 1.09 g/cm^3 for P(HOSt-tBA-St) and 1.17 g/cm^3 for P(HOSt-AA-St), the weight fraction of ionic penetrant, and the molecular weight of the ionic penetrant. The density estimate for each polymer was based on an ideal mixing rule (additive volumes) using the densities of PHOSt (1.16 g/cm^3), PSt (1.04 g/cm^3), and PtBA (1.00 g/cm^3) or PAA (1.41 g/cm^3) homopolymers at 298 K. The spin rate was set to 2500 rpm to produce film thicknesses in the range of 200 to 300 nm. The feeder layer was baked at 383 K for 6 mins to remove residual PGMEA. Solvent removal as a function of time is reported in Appendix A in Figure A.5. Second, the diffusion layer was prepared by spin-casting the polymer from an 8 wt% solution in ethyl acetate (98% pure, Fisher Scientific) onto a polydimethylsiloxane (PDMS) stamp. The spin rate was set to 1500 rpm, producing a film thickness in the range of 600 to 1000 nm. The as-cast film on PDMS was solvent annealed under ethyl acetate vapor at room temperature for 1 hour to produce a smooth surface, then baked at 383 K for 6 min to remove excess solvent. Third, before allowing the stamp to cool, the diffusion layer on the PDMS stamp was placed into contact with the feeder layer on silicon using light pressure to bond the layers together. After holding for 15 sec, the PDMS stamp was carefully removed. Finally,

each bilayer sample was annealed in a nitrogen-purged chamber to activate diffusion of the ionic penetrant.

Characterization of Bilayer Thickness and Surface Roughness. The thicknesses of the base layer and the bilayer were measured with a J.A. Woollam M-2000 spectroscopic ellipsometer and analyzed using CompleteEASE software. The thickness of the top layer was determined by subtracting the base layer from the total bilayer thickness. The ellipsometry parameters Δ and Φ were modeled for a three layer system of polymer film, native oxide, and silicon (in air). The refractive index of the polymer was described by the Cauchy dispersion relationship, $n(\lambda) = A + B/\lambda^2$, where λ is the wavelength of incident light in units of nm. The refractive index of native oxide and silicon were fixed to known values that are built-in to the instrument software. The parameters A , B , and film thickness were optimized through regression analysis. Typical values of A and B were approximately 1.5 and 0.01, respectively. The surface roughness of each polymer film was evaluated using Atomic Force Microscopy (AFM), which confirmed that the surfaces were smooth. Procedures for surface roughness evaluation are provided in Appendix A along with representative AFM images (Figure A.6).

Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS). The ionic penetrant depth profile was analyzed using a TOF-SIMS NCS system, which combines a TOF.SIMS 5 instrument (ION-TOF GmbH, Münster, Germany) and an in-situ Scanning Probe Microscope (NanoScan, Switzerland). This instrument is managed by the Shared Equipment Authority at Rice University. The primary probe for analysis was bunched 30 keV Bi_3^+ ions with a measured current of 0.15 pA and a scanned area of $100 \times 100 \mu\text{m}^2$. Sputtering was performed using Ar_{1500}^+ ions at 10 keV with a typical current of 0.8 nA and a rastered area of $500 \times 500 \mu\text{m}^2$. The beams were operated in non-interlaced mode, alternating one analysis cycle and one sputtering cycle (corresponding to 1.63 s) followed by a pause of 5 s for charge compensation by flood exposure to an electron beam during the analysis. Adjustment of charge effects was performed using a surface potential of -95 V and

a extraction bias of -20 V for the negative polarity (i.e. negative SIMS mode). The cycle time was fixed to 200 μ s, corresponding to a mass range of $m/z = 0 - 3644$ amu.

Depth-Dependent Composition of Ionic Penetrants in Bilayers. TOF-SIMS data were collected in the form of ion signal versus sputter time. The three ion signals of interest were 1) Si^- , unique to the substrate; 2) F^- , unique to the ionic penetrants and substrate; and 3) $\text{C}_8\text{H}_7\text{O}^-$, unique to the polymers. Sputter depth was calculated from sputter time using the known bilayer thickness and the rapid rise in the Si^- signal, where the midpoint of this rise corresponds with the position of the polymer/silicon interface. The validity of this depth calibration was straightforward to test as there were weak Si^- signals at the free surface and at the interface between the bilayers due to trace contaminants, and the depth of the bilayer interface matched the known thickness of the top layer. The ion concentration was calculated from the ratio of F^- to $\text{C}_8\text{H}_7\text{O}^-$ signals, as this quantity is proportional to the number density of ion pairs ($\#/\text{nm}^3$) in either polymer (Figure A.7). While the F^- signal is also detected from the silicon wafer, there is no possibility that fluorine could leach from silicon into the polymer film (or vice versa) at the experimental temperatures. The calculations of ion concentration were validated in each data set by comparing the integrated number density of ions with the known amount of ions per unit area in the bilayer system.

3.2 Results

3.2.1 Glass transition of terpolymers

The effects of polymer chemistry, P(HOSt-tBA-St) versus P(HOSt-AA-St), on both density and glass transition temperature (T_g) were examined by a combination of atomistic simulations and experiments, with results presented in Figure 3.3. From simulations, the specific volume of P(HOSt-tBA-St) is found to be $\sim 10\%$ higher relative to P(HOSt-AA-St), which demonstrates that reaction will drive densification of the polymer matrix in proportion to the extent of deprotection. This is consistent with ellipsometry measurements

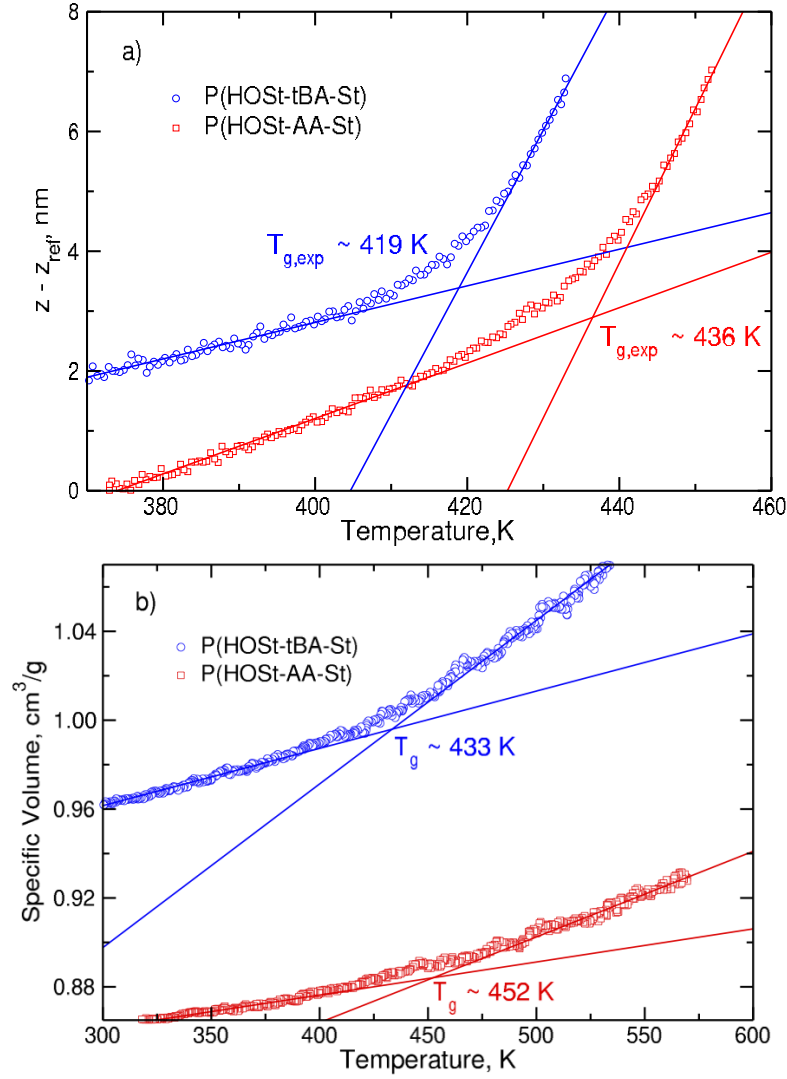


Figure 3.3: a) Film thickness (z) relative to a reference value (z_{ref}) as a function of temperature for P(HOST-tBA-St) (blue circles) and P(HOST-AA-St) (red squares), as probed through spectroscopic ellipsometry. Experimental glass transition values ($T_{g,exp}$) were obtained from the change in slope. b) Specific volume as a function of temperature of P(HOST-tBA-St) (blue circles) and P(HOST-AA-St) (red squares) from simulations. Glass transition values (T_g) were obtained from the change in slope.

of relaxed film thicknesses before and after reaction. As is typical in simulations, the T_g was approximated based on the point of intersection between linear models at low and high temperatures. The values calculated are 452 K for P(HOSt-AA-St) and 433 K for P(HOSt-tBA-St), respectively, which are approximately 16 K larger than the experimental T_g values determined from ellipsometry. While simulation estimates of T_g are not directly comparable to experiments, the trend with polymer chemistry and the magnitude of the discrepancy lend support to the models: The cooling rates in simulations and experiments were 10 K/ns and 10 K/min, respectively. Based on a simple estimate, higher cooling rates increase T_g by roughly 2 K per each order of magnitude.^[74] These simulations and experiments were repeated with the addition of 0.11 #/nm³ Na⁺TFL⁻ and no appreciable change in T_g was observed as a function of ion content at concentrations used herein.

The increase of T_g for P(HOSt-AA-St) relative to P(HOSt-tBA-St) can be rationalized through the presence of hydrogen bonding in these materials. Early literature studies with P(HOSt-St) random copolymers established the role of hydrogen bonds in elevating the T_g .^[75, 76] According to these studies, a 25 mol% increase in HOSt composition from 55 mol% to 80 mol% would lead to a 20 K increase in T_g .^[75] In our terpolymers, the tBA repeat units in the protected terpolymer can only perform as hydrogen bond acceptors,^[77] and deprotection of tBA to AA provides additional hydrogen donor and acceptor sites due to the carboxyl group.

3.2.2 Ion-polymer interactions

The P(HOSt-tBA-St) and P(HOSt-AA-St) polymers each consist of three different type of repeat units bonded in a statistically random sequence. As a result, at length scales beyond 1 nm, ions experience an average environment representative of the average polymer composition. However, at shorter distances, preferential interactions favor proximity of ion pairs to specific moieties. Analysis of the molecular dynamics trajectories allows us to gain quantitative insight into the interactions between Na⁺TFL⁻ and the terpolymers.

Figure 3.4a provides the pair distribution functions of P(HOST-tBA-St) and P(HOST-AA-St) between the center of masses (COM) of the triflate anion and specific polymer repeat units. These data quantify the relative affinity of the anion to certain groups within a system (given the normalization to bulk density at far separations). The top panel of Figure 3.4a reveals that the anion in the P(HOST-tBA-St) system preferentially interacts with HOST and distances itself from tBA and St units to the extent that is permitted by covalent links in the copolymer. Both tBA and St exhibit a similar depletion at short distances with an enrichment at around 1.1 nm before converging to the average number density in the system. The bottom panel shows a similar preferential interaction in the P(HOST-AA-St) system, but the amplitude of these favorable interactions is reduced with AA units being a more favorable environment than tBA. Hence, the anion in the P(HOST-AA-St) matrix experiences a more “homogeneous” environment with AA units providing for an additional partner beyond the unfavorable St units. The nature of these favorable interactions can be traced to the ability of HOST and AA units to participate in hydrogen bonding as well as salt bridges via the Na^+ cation. These trends persisted across ion concentrations with noticeable changes as a function of temperature.

As observed in the simulation data in Figure 3.3b, the specific volume of P(HOST-tBA-St) presents a steeper decrease with temperature above T_g than P(HOST-AA-St), signifying a higher thermal expansion coefficient. While this is not evident in the experimental data of Figure 3.3b, the experiments encompass a narrow temperature range near T_g . A direct consequence of this difference between the two systems is that as temperature decreases and polymer repeat units pack at closer separations, favorable interactions within the P(HOST-tBA-St) increase at a higher pace. Using standard geometric criteria of a hydrogen-donor-acceptor angle cutoff of 30° and donor-acceptor distance cutoff of 0.35 nm, we calculated the number of hydrogen bonds per triflate anion between all triflate anions and polymer groups as a function of temperature and chemistry. These data, which are presented in Figure 3.4b, confirm that there is a larger number of hydrogen bonds formed in P(HOST-AA-St) relative to P(HOST-tBA-St). It is also clear that a decrease in temperature increases hydrogen bonding. However, as shown by comparing the number of hydrogen bonds in

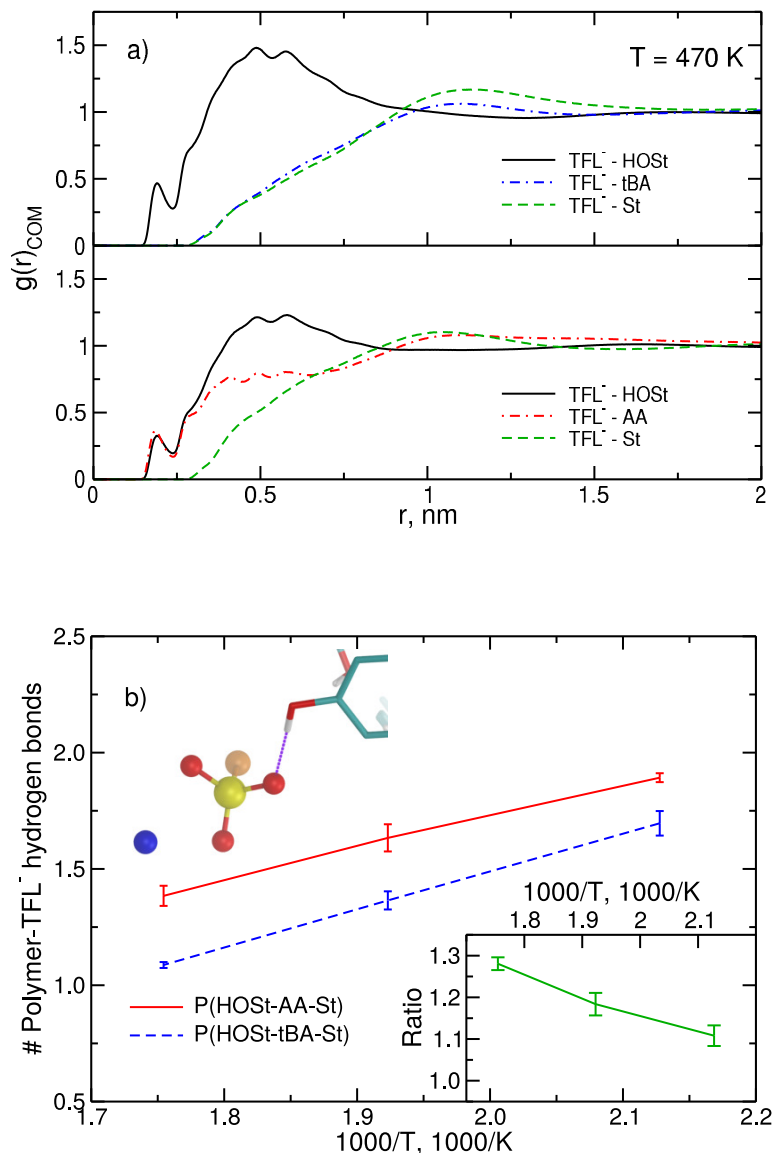


Figure 3.4: a) Pair distribution function between the COM of TFL^- anions to the COM of specific polymer groups for the system of $0.11 \text{ \#}/\text{nm}^3 \text{ Na}^+\text{TFL}^-$ at 470 K. Top panel refers to the $\text{P}(\text{HOST-tBA-St})$ system while the bottom panel refers to $\text{P}(\text{HOST-AA-St})$. b) Number of hydrogen bonds per TFL^- between TFL^- and polymer groups as a function of temperature and chemistry with $\text{P}(\text{HOST-tBA-St})$ in dashed blue and $\text{P}(\text{HOST-AA-St})$ in solid red and with $0.11 \text{ \#}/\text{nm}^3 \text{ Na}^+\text{TFL}^-$. Error bars correspond to a 95% confidence. The inset plot shows the number of polymer-anion hydrogen bonds in $\text{P}(\text{HOST-AA-St})$ relative to $\text{P}(\text{HOST-tBA-St})$ as a function of temperature.

each polymer matrix (inset), the difference diminishes as the temperature decreases. Similar trends were found for all ion concentrations. These preferential interactions and their change with temperature can impact diffusion in these materials as we present after discussing ion-ion interactions through the unique insight that molecular simulations offer.

3.2.3 Distribution of ions and ion-ion interactions

We quantified the extent of association of the TFL^- ions in our systems using a simple geometric criterion: cluster size that was calculated based on the number of TFL^- ions within a 0.75 nm radial distance of a TFL^- , inclusive of the reference TFL^- , where distances were determined between their respective centers of mass. Note that dissociated Na^+ and TFL^- ions were not observed in any of our systems. The multi-microsecond long trajectories allowed for a reliable examination of the propensity to form clusters, irrespective of the initially random placement, even at the lowest temperature studied. Figure 3.5a presents the effects of polymer chemistry on clustering of Na^+TFL^- at a concentration of $0.11 \text{ \#/nm}^3$ and 470 K. The inset shows the average cluster size as a function of time for each material, where values shown in the main figure were extracted from the long-time plateau. The probability distribution for the ion concentration of $0.11 \text{ \#/nm}^3$ at 470 K reveals that the ionic penetrant will cluster into dimers and trimers in both P(HOSt-tBA-St) and P(HOSt-AA-St) , but P(HOSt-tBA-St) has more trimers (and fewer dimers) than P(HOSt-AA-St) . The same trend, that the ionic penetrant shows an increased propensity for higher-order clustering in P(HOSt-tBA-St) as compared to P(HOSt-AA-St) under the same conditions, is upheld for all the temperatures and concentrations that were considered in this study. These outcomes suggest that during a deprotection reaction, the formation of higher-order aggregates could be suppressed by conversion of P(HOSt-tBA-St) to P(HOSt-AA-St) , as the latter offers more repeat units for favorable interactions. However, as higher-order aggregates are far less prevalent than single ion pairs and dimers, which make up the majority of ionic penetrant states, their impact could be minimal.

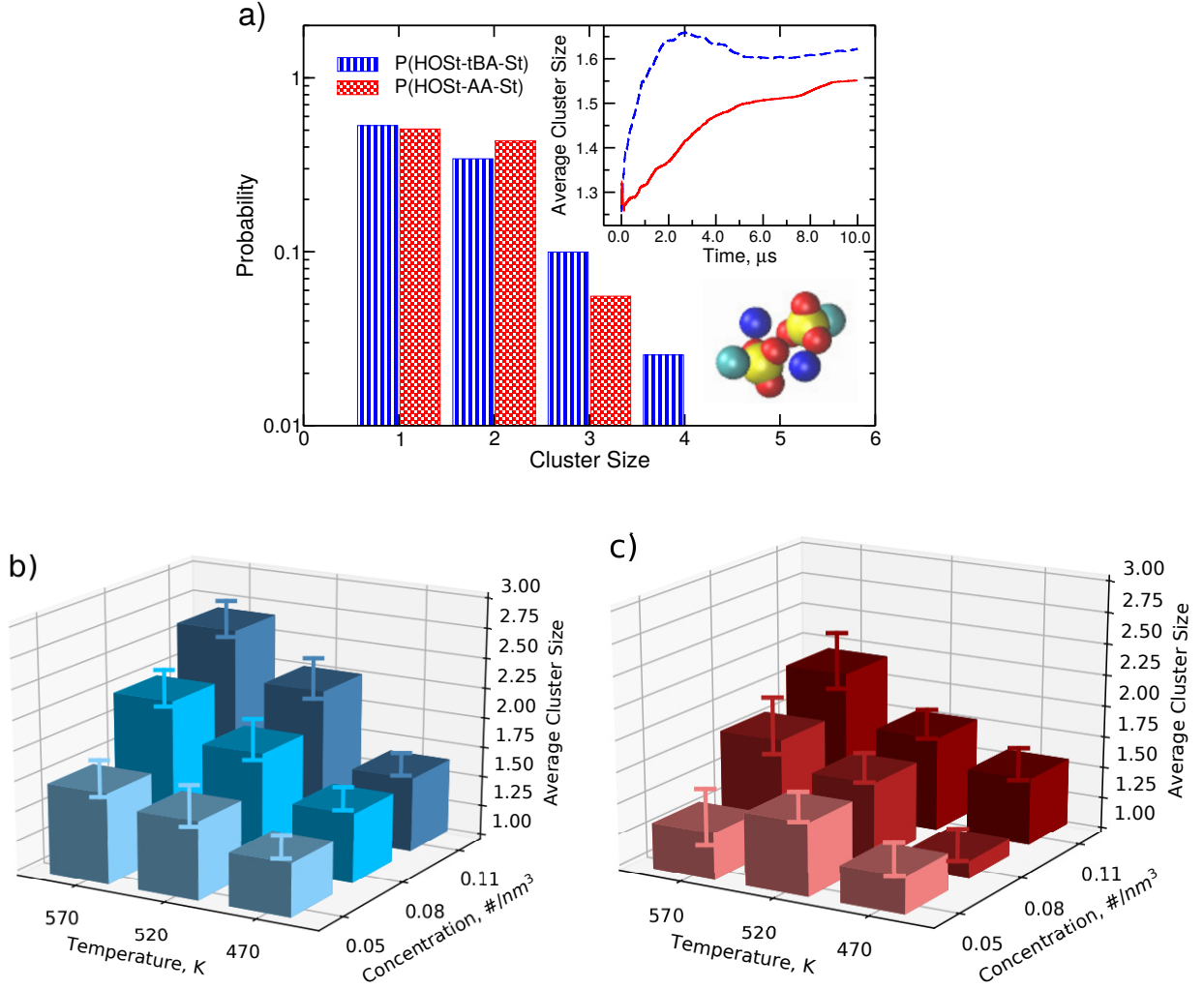


Figure 3.5: a) Distributions of ionic penetrant cluster size in P(HOST-tBA-St) (dashed blue) or P(HOST-AA-St) (solid red) with 0.11 #/nm³ Na⁺TFL⁻ at 470 K. Inset reports average cluster size versus simulation time. Visualization of typical cluster of size 2 is provided. b) Equilibrium average cluster size as a function of temperature and ion concentration for P(HOST-tBA-St). c) Equilibrium average cluster size as a function of temperature and ion concentration for P(HOST-AA-St). All error bars correspond to a 95% confidence interval.

The effects of temperature and ion concentration on equilibrium average cluster size in P(HOSt-tBA-St) and P(HOSt-AA-St) are shown in Figures 3.5b and 3.5c, respectively. Equilibrium average cluster size is defined as the time average of average cluster size for the last half of each trajectory, and error bars are calculated using a 95% confidence interval of these averages. At all conditions, the equilibrium average cluster size is the same or slightly reduced in P(HOSt-AA-St) when compared to P(HOSt-tBA-St). Furthermore, within each material, the equilibrium average cluster size is depressed as ion concentration and temperature are reduced. In P(HOSt-AA-St), the average cluster size shows non-monotonic dependencies on ion concentration at a fixed temperature of 470 K and on temperature for a fixed ion concentration of $0.05 \text{ \#}/\text{nm}^3$. However, because of the low temperature and/or low ion concentration, the statistical error in these data is high. Therefore, these trends should be interpreted with caution. The effect of concentration on equilibrium average cluster size is not surprising, as higher-order interactions are less probable as their concentration is decreased. The effect of temperature on clustering is more counter-intuitive: one might anticipate a decrease in clustering at high temperature, where entropy favors single ion pairs, rather than a decrease at low temperature. This outcome points toward an enhanced solubility of the ionic penetrants at lower temperatures, potentially due to ions with decreased kinetic energy spending more time in regions of higher polarity, as well as the increased proximity of favorable repeat units due to the higher density. Deprotection reactions are commonly performed at low temperatures (below the glass transition). Therefore, if solubility of the ion pairs increases as temperature is reduced, then irreversible aggregation is not likely to contribute to suppressed reaction kinetics at long times.

In principle, the extent of clustering could affect dynamics, as clusters should diffuse more slowly than individual ion pairs due to their larger effective size. However, such behavior is difficult to quantify because the individual ions do not stay in the same cluster state for the duration of the simulation, but are continuously combining, separating, and redistributing among different clusters. Our data suggest that the plateau in deprotection level observed in CARs does not represent strong catalyst-catalyst interactions forming irreversible aggregates,

but rather a dynamic picture emerges where ion pairs are able to transition between single states and higher-order clusters throughout the course of the simulations.

3.2.4 Ion dynamics

In this section, we examine the ion transport in our systems as probed by detailed atomistic simulations and TOF-SIMS experiments. The effects of polymer chemistry, temperature, and Na^+TFL^- concentration on Na^+TFL^- transport in NVT simulations are summarized in Figure 3.6. The dynamics of the Na^+TFL^- ion pairs are quantified by analyzing displacements of the COM of TFL^- ions. This metric suffices to examine transport of the ion pair since we observed that Na^+ always remained in proximity of the anion, and the mobility of the latter controls the overall diffusion process in our materials. The dynamic behavior of the TFL^- ions exhibits significant heterogeneities and jump-like mobility, reminiscent of transport in glassy materials as quantified through single particle tracking. Figure 3.6a presents single particle displacements of two selected TFL^- anions from an NVT simulation at the lowest temperature studied (470 K) with a Na^+TFL^- loading of $0.11 \text{ \#}/\text{nm}^3$. While one anion is immobile, aside from exhibiting vibrational motion throughout the course of the simulation, a different anion is able to explore a significant part of the simulation volume. This jump motion persists across both polymer chemistries, all ion concentrations, and all temperatures. At higher temperatures eventually all TFL^- become mobile hence no memory of initial placement persists. We attribute these features to the strong directional interactions with multiple HOST monomers, which produces a strong barrier to translation, even at temperatures far from T_g .

While translation can occur via disruption of specific interactions with polymer repeat units, and successive formation of new ones, the polymer itself also shows appreciable mobility at the temperatures studied with simulations. Figure 3.6b shows the effects of temperature on the mean square displacement (MSD) of the TFL^- anions in P(HOST-AA-St), along with the MSD for P(HOST-AA-St) as a reference. (The data for P(HOST-AA-St) at 470 K reflect the dynamics of the slowest system at the lowest temperature, and are

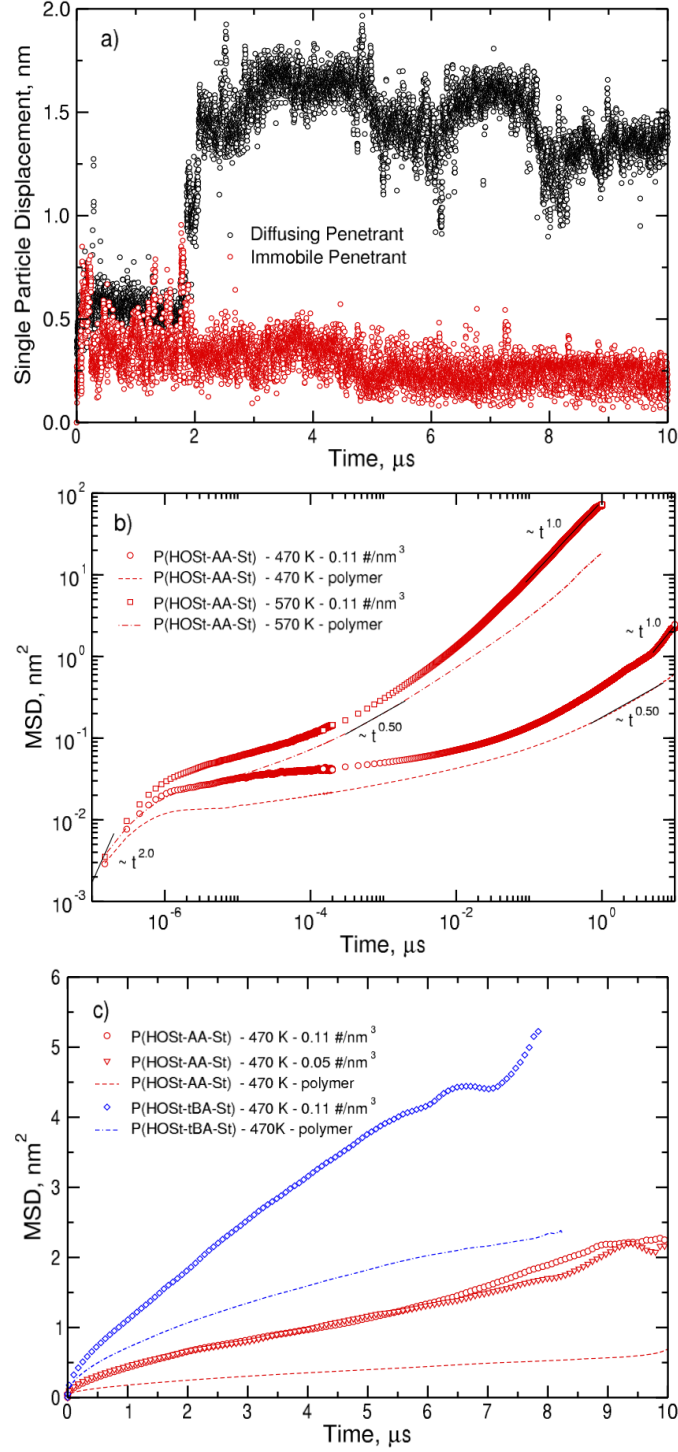


Figure 3.6: a) Single-particle displacement of two selected TFL⁻ anions in P(HOST-AA-St) at the lowest temperature studied (470 K) and 0.11 #/nm³. b) Average MSD of TFL⁻ in P(HOST-AA-St) and P(HOST-AA-St) at 470 K and 570 K (symbols). c) MSD of TFL⁻ in P(HOST-AA-St) at ionic penetrant concentrations of 0.05 #/nm³ and 0.11 #/nm³, and MSD of TFL⁻ in P(HOST-tBA-St) at 470 K for an ionic penetrant concentration of 0.11 #/nm³. Dashed lines represent the average MSD of polymer atoms in the respective systems.

provided as a lower-bound of our simulations.) Each MSD scales with a power-law in time, i.e. $\text{MSD} \propto t^n$, with a different exponent n depending on the time scale that is probed. These changes in scaling reflect differences in the diffusion mechanism: ballistic motion for $n = 2$, anomalous sub-diffusion for $n < 1$, Rouse motion for $n = 0.5$, and Fickian motion for $n = 1$.^[78] At 570 K, it is evident that the polymer experiences significant segmental mobility ($n = 0.5$) and even a diffusive regime during the course of the simulation. An analysis of chain center-of-mass dynamics and the end-to-end vector autocorrelation function for the slowest terpolymer, P(HOSt-AA-St), together with estimates of the monomeric friction coefficients and comparison to polystyrene,^[78,79] are presented in Appendix A in Figures A.3 and A.4. At the highest temperatures studied, a complete decorrelation from the starting configuration is observed. At the lowest temperature studied, chains do not fully relax. Another observation is that the TFL⁻ anion short-time dynamics appear to follow a similar trend to that of the terpolymer segments. This suggests that ion pairs undergo a dynamic coupling/decoupling with the terpolymer segments over the course of the simulation. This general trend is observed for all chemistries, ion concentrations, and temperatures. The TFL⁻ anion shows ballistic motion at short-times, then anomalous diffusion at intermediate times, and finally Fickian diffusion in the long-time limit. The anomalous anion dynamics that become Fickian are a consequence of the heterogeneous behavior and jump-like motion shown in Figure 3.6a.^[80] Eventually, as we approach T_g , long-range motion of the polymer is suppressed. We could identify a diffusive regime for the TFL⁻ anions at 470 K, but this was not the case for the polymer matrix which experienced solely segmental mobility. While the MSD for TFL⁻ anions signals Fickian diffusion on the average, the mechanism is quite heterogeneous as shown in Figure 3.6a.

The ion dynamics differ significantly between the two polymer chemistries studied. MSDs of TFL⁻ at 470 K, along with the MSD for each polymer as a reference, are shown in Figure 3.6c. TFL⁻ undergoes larger displacements in P(HOSt-tBA-St) than in P(HOSt-AA-St). This trend holds for all ion concentrations and temperatures, and is consistent with the different densities of the two polymers, as the increased density of P(HOSt-AA-St) relative to P(HOSt-tBA-St) is expected to suppress the diffusivity of Na⁺TFL⁻. This

trend is also consistent with the difference in matrix polarity, as the higher polarity of P(HOSt-AA-St) could be expected to interact with the ion pair and limit diffusion, but this is less likely as HOSt is the strongest interacting group and is present in the same proportion in both terpolymer chemistries. Figure 3.6c also shows that the MSD of TFL⁻ in P(HOSt-AA-St) is independent of Na⁺TFL⁻ concentration. The same is true for TFL⁻ in P(HOSt-tBA-St), and this trend holds across all the temperatures and concentrations that were studied. Even though it was shown that increasing Na⁺TFL⁻ concentration corresponds to a small increase in Na⁺TFL⁻ clustering, it seems that this difference in clustering does not produce an appreciable change in the calculated MSD. We expect that the majority of ionic penetrants diffuse as either individual ion pairs or dimers. Finally, the calculated MSDs allow for estimates of the the diffusivity, D , of Na⁺TFL⁻ within each polymer matrix by linear regression on the long-time behavior, which should present a slope proportional to $6D$. These diffusivities were extracted for each temperature, ion concentration, and polymer matrix chemistry, and are compared to experiments later in Figure 3.8 and in our discussion.

Despite our multi-microsecond long trajectories, the lowest temperature accessible by atomistic simulations was limited to 470 K, which is at least 50 K above T_g . At even lower temperatures, most of the TFL⁻ anions remain relatively immobile throughout exceedingly long simulation times (over 10 μ s), rendering the extraction of transport properties very challenging. On the other hand, experimental techniques such as TOF-SIMS can measure diffusion lengths at the scale of 10-1000 nm. Therefore, TOF-SIMS was used to probe diffusion of Na⁺TFL⁻ in each polymer for temperatures in the range of 380-420 K. An example of TOF-SIMS data is presented in Figure 3.7 for Na⁺TFL⁻ in P(HOSt-AA-St). The control data were measured from an as-prepared bilayer and were used to determine the initial distribution of ionic penetrant throughout the total bilayer thickness. While the control data should exhibit a step-function concentration profile, as shown in the inset cartoon, the resolution limit of the TOF-SIMS experiment leads to broadening at the bilayer interface. Therefore, the control data were modeled by convolving a step-function concentration profile with a Gaussian resolution function, where the interface position z_1 and total depth z_2 are known and the Gaussian standard deviation was an adjustable parameter

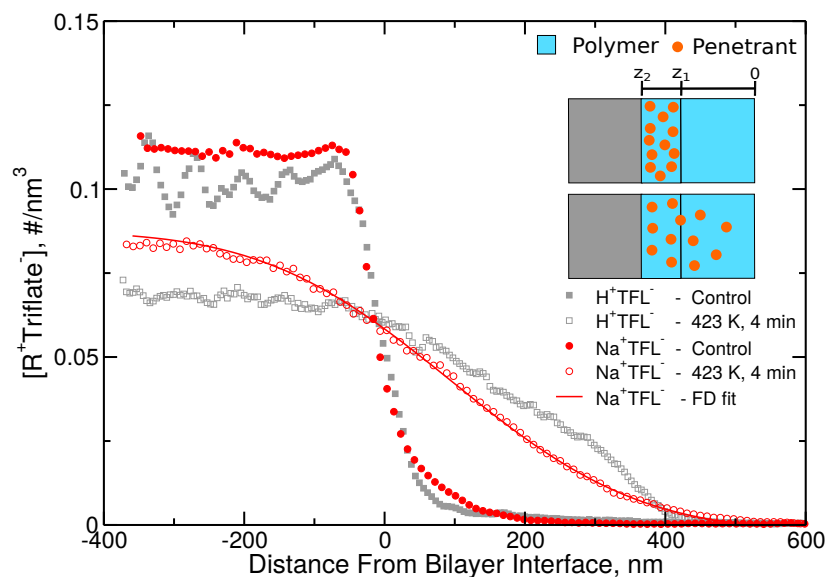


Figure 3.7: Representative TOF-SIMS data for as-prepared (control) and annealed bilayer samples of ionic penetrants in P(HOST-AA-St) in the form of number density vs depth from the bilayer interface. The inset graphic illustrates the distribution of ionic penetrant through the as-prepared and annealed bilayers, where z_1 and z_2 designate the depth of the interface (~ 600 nm) and the total depth of the film (~ 1000 nm), respectively, relative to the free surface.

for optimization. The post-annealing data were used to calculate a diffusivity for the ionic penetrant as a function of polymer chemistry, temperature, and concentration of Na^+TFL^- in the feeder layer. These data were modeled by integrating Fick’s second law with the finite differences method, where the initial concentration profile and resolution function for the final distribution were specified based on analysis of control data. The Fickian diffusivity, D , was an adjustable parameter for optimization. A detailed description of the model is provided in Appendix A along with all TOF-SIMS data and fits in Figures A.8 and A.9.

In addition to probing Na^+TFL^- diffusion with TOF-SIMS, we also examined the transport of H^+TFL^- (active catalyst) in P(HOSt-AA-St). These studies were used to establish that the inert Na^+TFL^- penetrant is a reasonable analogue to the exact catalytic compounds used in reaction-diffusion processes. The TOF-SIMS data shown in Figure 3.7 demonstrate that the diffusion length for Na^+TFL^- in P(HOSt-AA-St) is similar to that of H^+TFL^- . However, the shape of the H^+TFL^- diffusion front does depart from the profile generated by integration of Fick’s second law. The H^+TFL^- penetrant is generated through a light-induced decomposition of the photoacid generator, as described in the procedures and elsewhere,[3, 81, 82] which generates several byproducts that remain in the film. These byproducts may diffuse along with the H^+TFL^- penetrant, thereby plasticizing the polymer and altering the shape of the diffusion front.[83] One might anticipate that co-diffusion of H^+TFL^- and acid generation byproducts would increase the overall diffusivity of the H^+TFL^- relative to Na^+TFL^- , but the depth of the diffusion front is similar for both ionic penetrants.

The diffusivities from atomistic simulations and from TOF-SIMS experiments are summarized in Figure 3.8. Each data point is a diffusivity value that was extracted from a single simulation or experiment. The symbol size spans a range of approximately half to double the central value, larger than the associated uncertainty in the determination of D , therefore error bars are not shown. Simulations predict that diffusion is slower in P(HOSt-AA-St) than in P(HOSt-tBA-St) at higher temperatures. We reported earlier that P(HOSt-tBA-St) densifies more rapidly with quenching, and differences in ion-polymer interactions between the two polymeric systems appear to decrease. This point is supported by experiments, where ion diffusivity in each polymer chemistry is similar at temperatures

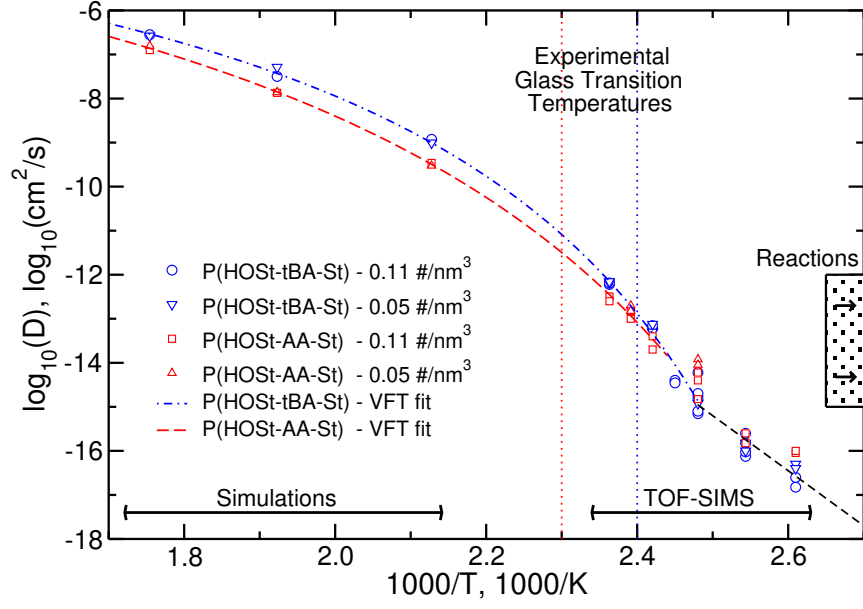


Figure 3.8: Diffusivities from MD simulations (high T) and TOF-SIMS experiments (low T). Dashed lines are best-fit to a VFT model at $T > T_g - 20$ K. An Arrhenius line for data in both P(HOST-tBA-St) and P(HOST-AA-St) is drawn with a dashed line for $T \ll T_g$. A shaded rectangular area provides a visual representation of values commonly extracted with mesoscopic reaction-diffusion models targeting deprotection reactions CAR materials. Vertical dotted lines denote T_g for each polymer.

near and below the glass transition. It has been proposed that the observed trapping in reaction-diffusion models could be a product of greater interactions between the catalyst and deprotected polymer,^[13] but our findings suggest that interactions with HOS_t are limiting diffusion in both materials. Another major outcome of our study is that both simulations and experiments show that the diffusivity is independent of ion concentration, so any deviations from a linearly dependent “trapping model” should be examined within the context of local changes induced by the reaction.

For each polymer chemistry, the combined data from simulations and experiments are well-described with a single master curve following the Vogel-Fulcher-Tammann (VFT) equation,^[84]

$$D(T) = D_0 \exp \left(\frac{A}{T - T_r} \right) \quad (3.1)$$

where $D(T)$ is diffusivity (cm²/s) and D_0 (cm²/s), A (K), and T_r (K) are adjustable parameters. While the short quenching simulations (300 K/30 ns) produced T_g values that were elevated relative to experiments, this is anticipated given that cooling rates in simulations were orders of magnitude higher than those in experiments. Therefore, simulation data at high temperatures and experimental data at low temperatures are plotted together without any shift factors. The VFT model is valid for temperatures near and above T_g so the fit was restricted to $T > T_g - 20$ K. The optimized VFT parameters for Na⁺TFL⁻ in P(HOS_t-tBA-St) are $D_0 = 5.42 \times 10^{-4}$ cm²/s, $A = 1750$ K, and $T_r = 338$ K. The optimized VFT parameters for Na⁺TFL⁻ in P(HOS_t-AA-St) are $D_0 = 1.38 \times 10^{-3}$ cm²/s, $A = 2320$ K, and $T_r = 318$ K. For the self-diffusion of a polymer melt, the parameter T_r is typically near $T_g - 50$ K. The estimated T_r values for self-diffusion of P(HOS_t-tBA-St) and P(HOS_t-AA-St) are 360 K and 380 K, respectively, and neither the trend with polymer chemistry nor the magnitudes of these values are in agreement with the VFT analysis. However, there are several reasons (beyond uncertainties in data extraction) why T_r in these systems should differ from these predictions. First, the VFT model in Figure 3.8 is applied to diffusion of ionic penetrants within the polymer matrix, rather than polymer self-diffusion. MSD analysis of simulated trajectories showed that penetrant motion was decoupled from that of

the polymer matrix (Figure 3.6b-c), and was also accelerated relative to the polymer. Second, the estimated T_r does not account for the increased solubility of Na^+TFL^- penetrant in P(HOSt-AA-St) compared with P(HOSt-tBA-St), which leads to fewer higher-order clusters in the former system (Figure 3.5). As clusters of ion pairs are presumed to diffuse more slowly than the individual penetrants, this behavior could account for the lower T_r of P(HOSt-AA-St) relative to P(HOSt-tBA-St). Finally, the solubility of ionic penetrants in both polymer chemistries was increased with reductions in temperature, thereby suppressing clustering and depressing T_r .

At temperatures below $T_g - 20$ K, the diffusivities of ionic penetrants in both polymers roughly follow the same Arrhenius temperature dependence, which is typical of penetrant diffusion in glassy polymers.[85, 86, 87] The Arrhenius prefactor and activation energy are approximately 10^{16} cm^2/s and 230 kJ/mol, respectively. The critical question pertaining to our findings is how these data fit within the context of the reaction-diffusion mechanisms, where processing temperatures below the glass transition are employed in commercial lithography. As shown in Figure 2.3, when deprotection kinetics are analyzed with mesoscopic reaction-diffusion models that depend solely on a constant diffusivity, D , the optimized value of $D \sim 10^{-16}$ cm^2/s exceeds our measured values by two orders of magnitude,[13, 17, 22, 27, 42, 45, 47] albeit with similar activation energies. The recent molecular dynamics study by Kim and co-workers extracted values on the order of 10^{-14} cm^2/s for acid-anion diffusion in a similar CAR system, but they analyzed trajectories over short intervals (a few nanoseconds) where sampling is inadequate to represent Fickian diffusion.[43] The catalyst transport mechanism at short times might be more accurately described as subdiffusive rather than Fickian, as suggested in prior work.[45]

The data presented herein demonstrate that long-range diffusion in either the protected reactant, P(HOSt-tBA-St), or the deprotected product, P(HOSt-AA-St), is too slow to drive the deprotection kinetics, so a mechanism of local enhancement needs to be identified. Several hypotheses can be posed to explain the local enhancement but none can be directly tested by our data. Byproducts of the photoacid generator decomposition reaction may cause plasticization of the polymer that enhances catalyst transport rates. However, in one of our

prior works,[88] we demonstrated that a 10 wt% loading of a common plasticizer in a similar CAR system increased diffusivities by roughly 70%, and this is too small of an increase to account for the difference between our inert model system and prior studies of reactive CAR systems. Additionally, the deprotection reaction produces a volatile byproduct (2-methylpropene) that rapidly escapes from the film.[20] If 2-methylpropene removal is a much faster process than polymer densification, then the free volume generated as 2-methylpropene is released from the film can decrease the local density of the polymer around the catalyst. This will accelerate diffusion of the ions above diffusivities expected in a relaxed polymer, but should revert to these expected diffusivities as the polymer relaxes to release the free volume.[19]

While our molecular simulations and TOF-SIMS experiments do not address transport in the presence of the reaction, we believe that the findings add further insight into the role of diffusion in deprotection kinetics. As described in the introduction, several studies introduce a “trapping” or acid-loss mechanism to capture the limited conversion of the reactant at long-times.[13, 15, 28, 43] To demonstrate this saturation in conversion, Figure 3.9 presents experimental deprotection kinetics of P(HOSt-tBA-St) at 350 K for two concentrations of H^+TFL^- catalyst. The experimental data are compared with predictions of deprotection levels, denoted as pseudo-reaction, based on a Kinetic Monte Carlo model of instantaneous reaction coupled to Fickian H^+TFL^- diffusion with a box discretization of 1 nm, as described in our prior publication.[45] The prediction for 470 K was based on a catalyst diffusivity of $3.5 \times 10^{-10} \text{ cm}^2/\text{s}$, which was obtained from the MD trajectory of Na^+TFL^- in P(HOSt-AA-St) at a concentration of $0.11/\text{nm}^3$. The prediction for 350 K was based on a catalyst diffusivity of $1 \times 10^{-18} \text{ cm}^2/\text{s}$, which was estimated by extrapolation of the experimental data points in Figure 3.8 using the Arrhenius temperature dependence. The experimental deprotection rate is found to be roughly 2 orders of magnitude faster than the predicted rate at 350 K, which further underlines the disparity between the diffusivity extracted when fitting reaction data and when probing inert equilibrium materials. It can also be seen that the apparent plateau in experimental deprotection level at long timescales overlaps with the onset of limited diffusion in an inert material. This outcome suggests that in CARs with volatile

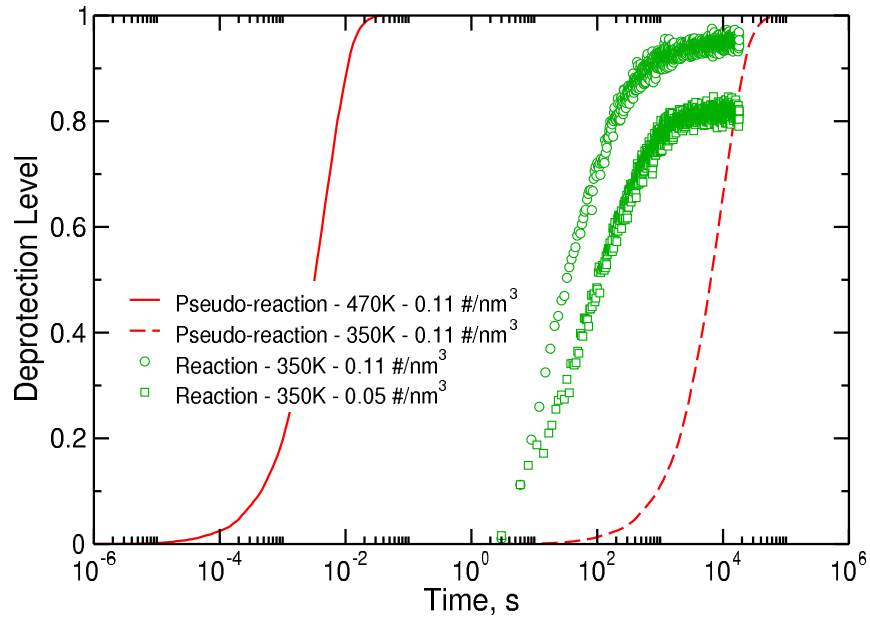


Figure 3.9: Deprotection level versus time for pseudo-reaction dataset of P(HOSt-AA-St) with $0.11 \text{ \#}/\text{nm}^3$ Na^+TFL^- at 470 K ($D = 3.5 \times 10^{-10} \text{ cm}^2/\text{s}$) and, using the Arrhenius fit, extrapolated to 350 K ($D = 1 \times 10^{-18} \text{ cm}^2/\text{s}$). Experimental reaction kinetics at 350 K with H^+TFL^- concentrations of 0.05 and $0.11 \text{ \#}/\text{nm}^3$. Experimental reaction data show enhanced rates compared to pseudo-reaction at 350 K.

protecting groups, material relaxation following reaction might account for some of the apparent trapping. Given that average ion diffusivity appears to be independent of ion concentration, we hypothesize that the concentration-dependent plateau is linked to local enhancements due to reaction. However, this point needs to be addressed through future studies.

3.3 Conclusions

We presented a concerted experimental and modeling effort to examine ion pair diffusion in a model CAR resin of P(HOSt-tBA-St), which is deprotected to P(HOSt-AA-St) in the presence of an acid catalyst. We employed an inert catalyst analogue (Na^+TFL^-) to simulate the long-time ion dynamics with atomistic detail and to measure the diffusion profile with TOF-SIMS. This choice of system allowed us to examine the effects of polymer chemistry, ion concentration, and temperature on ion diffusivity in the absence of reaction. While Fickian transport is slightly accelerated in P(HOSt-tBA-St) relative to P(HOSt-AA-St) in simulations at high temperatures, both modeling and experiments demonstrate that differences in diffusivities and their temperature dependence are minimal as we approach the glass transition. We attribute this outcome to a diffusion process that is dominated by interactions with the HOSt units, which are present in each terpolymer. Therefore, given that reactions are commonly executed in the glassy state, our data suggest that ion diffusion in this terpolymer resin does not depend on composition (i.e. conversion). In addition, we measured bulk reaction kinetics with FTIR and compared to mesoscopic reaction-diffusion models based on the diffusivity in inert materials. As noted in early studies of other CAR systems, the diffusivities determined from reaction-diffusion models are significantly enhanced relative to the diffusivities in inert systems. We also find that transport in the inert materials aligns with the decelerated reaction rate that is often modeled with phenomenological trapping processes, but further studies are needed to determine if trapping can be solely ascribed to volume relaxation following the reaction. With that in mind, simulations that model deprotection events and capture material relaxation could inform the development

of reaction-diffusion models. Finally, the atomistic simulations demonstrate that ion-ion interactions do contribute to the observed dynamics, and to a greater extent in the more hydrophobic material P(HOSt-tBA-St) and at higher temperatures. However, the impact on average ion dynamics is minimal, so any deviations in reaction kinetics from a first-order dependence on catalyst concentration likely originates from transient states prior to material relaxation.

Chapter 4

Transient diffusion states during reaction

Our prior study demonstrated that the composition of the polymer and catalyst concentration do not have a significant impact on catalyst diffusion in the absence of reaction. However, catalyst diffusion during reaction is significantly enhanced compared to diffusion in the absence of reaction.[25,89] Some hypotheses on the origins of this enhancement include: 1) Plasticization of the polymer due to byproducts of the deprotection reaction and/or of photoactivation;[8,17,45,88,90] 2) The generation of excess free volume as volatile reaction byproducts quickly escape the glassy film.[10,17,19,45,88] One study probed these hypotheses in PtBOCSt and concluded that byproduct volatilization and polymer densification occur at much faster rates than reaction,[20] but it is unclear if these findings can be generalized to other CAR systems.

The goal of this study was to test hypotheses on the origins of accelerated catalyst mobility during reaction. We hypothesize that accelerated catalyst mobility during reaction is caused by local transient states that are produced by the scission and removal of protecting

Author notes: Parts of this chapter are adapted from C. M. Bottoms, G. E. Stein, and M. Doxastakis, “Transient diffusion states during reaction in chemically amplified resists,” 2022 Manuscript submitted for publication in special issue of Journal of Physical Chemistry A.

groups. Experiments to directly quantify local changes in chemistry and density of the polymer during reaction are difficult to perform and it is even more difficult to quantify the affects of such features on catalyst diffusivities and reaction rates. Therefore, we implement atomistic simulations of protecting group removal to model transient material states produced by reaction, assuming the instantaneous escape of reaction byproducts. These simulations allow us to determine the impacts of this removal on catalyst dispersion, excess free volume generation, and material densification and their resultant impacts on catalyst diffusivities.

4.1 Methods

4.1.1 Simulations

Models and Forcefields. This study uses forcefields that were priorly adapted to simulate catalyst diffusion in the absence of reaction.[89] A united atom description of the triflate counter-anion (TFL^-) paired with the sodium cation (Na^+) was obtained from Zhong et al.[58] The TraPPE-United-Atom forcefields of the protected polymer and the deprotected polymer were adopted from prior literature where non-polar hydrogens are lumped with directly connected carbon atoms.[62, 63, 64, 65] The united atom description of the system increases simulation efficiency allowing us to achieve the long trajectories necessary to characterize ion pair dynamics.

Software and Algorithms. In similar manner to our prior literature,[89] atomistic molecular dynamics simulations were conducted using GROMACS 2018.1.[68] Integration was performed using the leap-frog algorithm with a timestep of 1.5 fs.[69] The LINCS bond constraint algorithm was employed.[70] The Verlet neighbor list with a cutoff of 1.4 nm was employed for Van der Waals interactions. Electrostatics were included using the smooth Particle-Mesh Ewald algorithm.[71] The the stochastic velocity rescale method maintained

temperatures at the desired values.[72] Pressure coupling was performed using the Berendsen algorithm.[73]

Initialization. Initial ion pair and polymer configurations were selected from previous equilibrium simulations of Na^+TFL^- dynamics in the protected polymer and the deprotected polymer.[89] Initial configurations of randomly dispersed Na^+TFL^- at concentrations of 0.05 and 0.11 $\#/\text{nm}^3$, corresponding to 0.20 and 0.48 ion pairs/chain for the protected polymer, at temperatures of 520, 470, and 420 K were obtained from the temperature ramp at a rate of 10 K/ns used to examine the glass transition of the protected polymer. Initial configurations of equilibrium clustered Na^+TFL^- at a concentration of 0.11 $\#/\text{nm}^3$ at temperatures of 520 and 470 K were obtained from the final configuration of the 5 and 10 μs NVT simulations, respectively.

Simulations With Material Relaxation. Simulations with material relaxation were performed using an “ad-hoc” method of approximating the change in material state due to reaction, that maintains the simulation efficiency of classical simulations. Similar methods have been commonly used to create configurations of highly cross-linked polymers.[91, 92]. A geometric “reaction” criterion was developed of Na^+ cations being within 5 Å of the double bonded oxygen of protecting groups in tBA. NPT simulations were performed on the aforementioned initial configurations with periodic checks for this reaction criterion (every 9, 45, and 225 ps for 520, 470, and 420 K, respectively). During the reaction check, every tert-butyl protecting group that satisfies the reaction criterion is removed and replaced with a bonded hydrogen. The replacement of the larger protecting groups produces a small amount of unoccupied volume which equilibrates as the simulation progresses. This method operates on the assumption that byproducts of reaction escape from the material much faster than catalyst diffusion from the reaction site and material relaxation, and does not simulate the energetics of the reaction. However, these approximations allow us to simulate the multiple μs of equilibration necessary to characterize the effects of material relaxation on Na^+TFL^- dynamics. Using the assumptions of the model, state-of-the-art central processing units, and

Nvidia graphics processing units these simulations were performed at rates of approximately 100 ns/day.

Trajectory Extending Kinetic Monte Carlo. Trajectory extending kinetic Monte Carlo (TEKMC) is a simple method of coarse-graining and extending trajectories of penetrant diffusion. It is commonly used to approximate long-time dynamics of penetrants in simulations of glassy polymer matrices.[32,93] TEKMC is performed by: 1) discretizing the simulation box into a number, d^3 , of cubic subcells of volume, l^3 , (where the subcell width, l , equals simulation cell width divided by d); 2) assigning the subcell occupancy of penetrants, based on their center of masses (COMs), at each time in a “wrapped” trajectory; 3) selecting a timestep of analysis (τ) that is a multiple of the timestep of the trajectory; 4) counting the number, and origin and destination, of transitions of penetrants between subcells in all configurations τ apart; 5) using these transitions to develop an origin and destination dependent matrix of transition probabilities; 6) using this probability matrix to perform a monte carlo simulation of these transitions with a fixed timestep of τ and box lengths of l ; and 7) repeating the process while optimizing τ and l to match modeled mean square displacements (MSDs) to the penetrant COM MSDs. In this framework, the corresponding origin-destination and destination-origin probabilities are averaged to maintain detailed balance. The dynamics extracted from TEKMC are reliant on the connectivity of the diffusion pathways, that are mapped onto the discretized lattice by the transition probabilities, and this allows TEKMC to predict dynamics at shorter times, where dynamics are often anomalous. Therefore, by optimizing the modeled dynamics to the short-time penetrant dynamics from simulations, TEKMC can extend the observed penetrant dynamics to Fickian lengthscales for the approximation of penetrant diffusivities.

There are a few important considerations for the application of TEKMC to our system. The trajectories of TFL⁻ anions are obtained from NPT simulations and therefore the simulation cell has a range of subcell widths for the same value of d . However, as described in detail in Section 4.2.3, the short trajectories chosen to be analyzed by TEKMC show only small changes in simulation volume. Therefore, we have chosen to keep d constant for

each time in the trajectory and set the box length of the Monte Carlo model step to be the average of the range of subcell lengths. In addition, to minimize artifacts due to penetrants quickly displacing at the boundaries of subcells, for each set of d and τ the method was performed on the original trajectory and on trajectories where the full system was shifted half l in either the x, y, or z dimensions. The final MSD for comparison to the shorter-time MSD of the COMs of penetrants is obtained from the average MSD of these four generated trajectories.

4.1.2 Experiments

Deprotection Reaction. Thin films of 0.05, 0.08, and 0.11 H^+TFL^- in the protected polymer were created following our priorly reported method (Chapter 2).[89] Films are exposed to UV-light, as previously described, to fully convert all TPS-TFL to H^+TFL^- with some assumed production of photoactivation byproducts.

Film Relaxation. Thin films of 0.11 $\#/\text{nm}^3$ H^+TFL^- in the protected polymer were created in the same manner as the films for previously described reaction kinetics measurements. The same spectroscopic ellipsometer and polarization model described in Chapter 3 were used to measure the ellipsometry parameters and extract film thickness as a function of thermal annealing time at 350 K using an in-situ heat cell.

4.2 Results

4.2.1 Length scales of reaction and diffusion

Before we could determine the impact of reaction and material relaxation on accelerated ion pair diffusion it was necessary to develop an understanding of what length scales are relevant in the context of the reaction. The length scales needed to achieve full deprotection within our simulation boxes were determined by analyzing the trajectories of Na^+TFL^- and tBA or AA groups in the protected and deprotected polymers.[89] The analysis was performed by tagging

the tBA or AA groups visited by the ion pair using a geometric reaction criterion, described further in the Section 4.1. For the protected polymer, the number of visited tBA groups (5 Å) was tracked as a function of simulation time and an effective deprotection level was calculated by dividing the number of visited groups by the total number of tBA. For the deprotected polymer, the effective deprotection was calculated in a similar manner but in reference to the AA groups. Figure 4.1a provides the development of the effective deprotection level as a function of polymer chemistry and Na^+TFL^- concentration. Effective deprotection occurs at similar timescales in the protected polymer and the deprotected polymer and occurs faster at higher Na^+TFL^- concentrations. Figure 4.1b provides the MSD of TFL^- COMs as a function of polymer chemistry and Na^+TFL^- concentration. Similar dynamics are observed for both concentrations of Na^+TFL^- in the deprotected polymer, and Na^+TFL^- dynamics are enhanced in the protected polymer when compared to the deprotected polymer.

Faster effective deprotection at higher Na^+TFL^- concentrations is expected from the higher number of Na^+TFL^- ion pairs. The faster Na^+TFL^- dynamics observed in the protected polymer (Figure 4.1b), without an observed increase in effective deprotection (Figure 4.1a), was shown to stem from preferential local interactions between Na^+TFL^- and groups other than tBA, in our prior work.[89] There could also be an impact of increased ion pair clustering, excluding some Na^+ cations from satisfying the geometric reaction criteria. Importantly, these results show that, at these concentrations, Na^+TFL^- ion pairs only need to diffuse a few nanometers to deprotect the majority of the simulation cell. Local heterogeneities within the material are expected to have an impact of short-range diffusion, which suggests that catalyst diffusion could be heavily altered through changes in these local heterogeneities induced by transient states generated by the reaction.

4.2.2 Simulation with material relaxation

Simulations with material relaxation were designed to examine the effects of the instantaneous removal of protecting groups, and subsequent material relaxation, on ion pair mobility. This simulation method introduces transient local heterogeneities in polymer

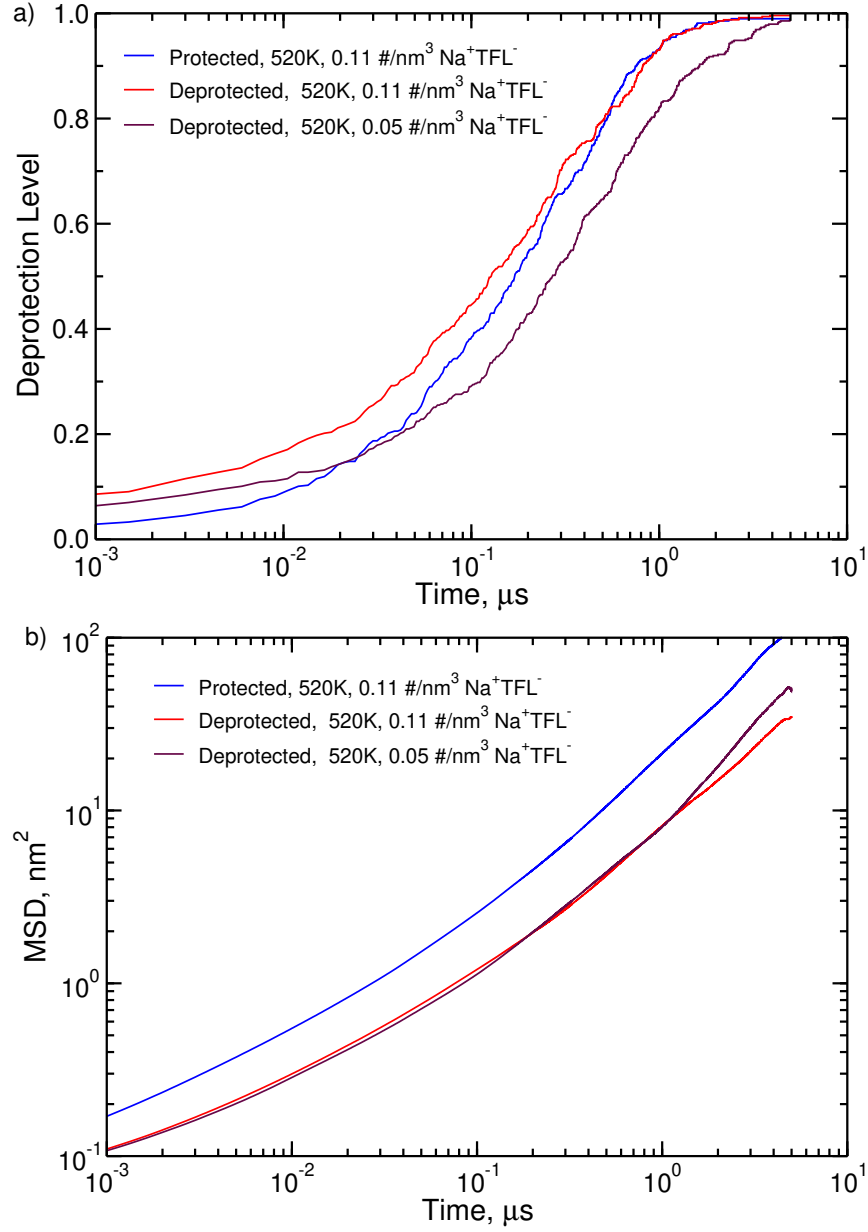


Figure 4.1: a) Effective deprotection level calculated from reaction group tagging for simulations of the protected polymer and the deprotected polymer with $0.11 \text{ \#/nm}^3 \text{ Na}^+\text{TFL}^-$ and for the deprotected polymer with $0.05 \text{ \#/nm}^3 \text{ Na}^+\text{TFL}^-$. b) MSDs of TFL⁻ COMs for these three conditions.

density and composition that are expected to impact ion pair and polymer mobilities and these heterogeneities are expected to evolve over time towards equilibrium. Figure 4.2a provides the deprotection level and volume loss over the course of a simulation with material relaxation at 520 K with $0.11 \text{ \#}/\text{nm}^3 \text{ Na}^+\text{TFL}^-$. The deprotection level is calculated by dividing the number of AA groups by the number of initial tBA groups. The volume loss is calculated by subtracting the simulation volume from the initial simulation volume. The timescales of deprotection are greatly enhanced when compared to the tagging of reaction groups in the absence of reaction, shown in Figure 4.1a. We also observe that global material relaxation, as reflected by volume loss, slightly lags relative to deprotection.

Comparison of the deprotection level and volume loss in simulations with material relaxation to the deprotection and thickness loss of reacting films suggests some differences between the two. Figure 4.2b reports the deprotection level, determined through FTIR, and the thickness loss, determined through spectroscopic ellipsometry, of thin films prepared with the protected polymer and $0.11 \text{ \#}/\text{nm}^3 \text{ H}^+\text{TFL}^-$. Deprotection level is calculated as described in Section 4.1 and the thickness loss is calculated by subtracting the film thickness from the initial film thickness. The rate of film thickness loss is significantly slower than the rate of deprotection. One contribution to this lag could be slower rates of material relaxation at experimental temperatures. At these temperatures, below the glass transition, the polymer chains are effectively immobile which limits the rate of thickness loss. In addition, our simulation method simplifies the reacting system through the assumption of the immediate escape of reaction byproducts. If generated reaction byproducts take time to escape from the film, this could also contribute to the observed lag. However, literature suggests that volatile reaction byproducts escape much faster than reaction-diffusion rates in a similar CAR chemistry.[20] While our simulation cannot capture material relaxation below glass transition, it does provide detailed data on the impact of material relaxation on catalyst diffusion.

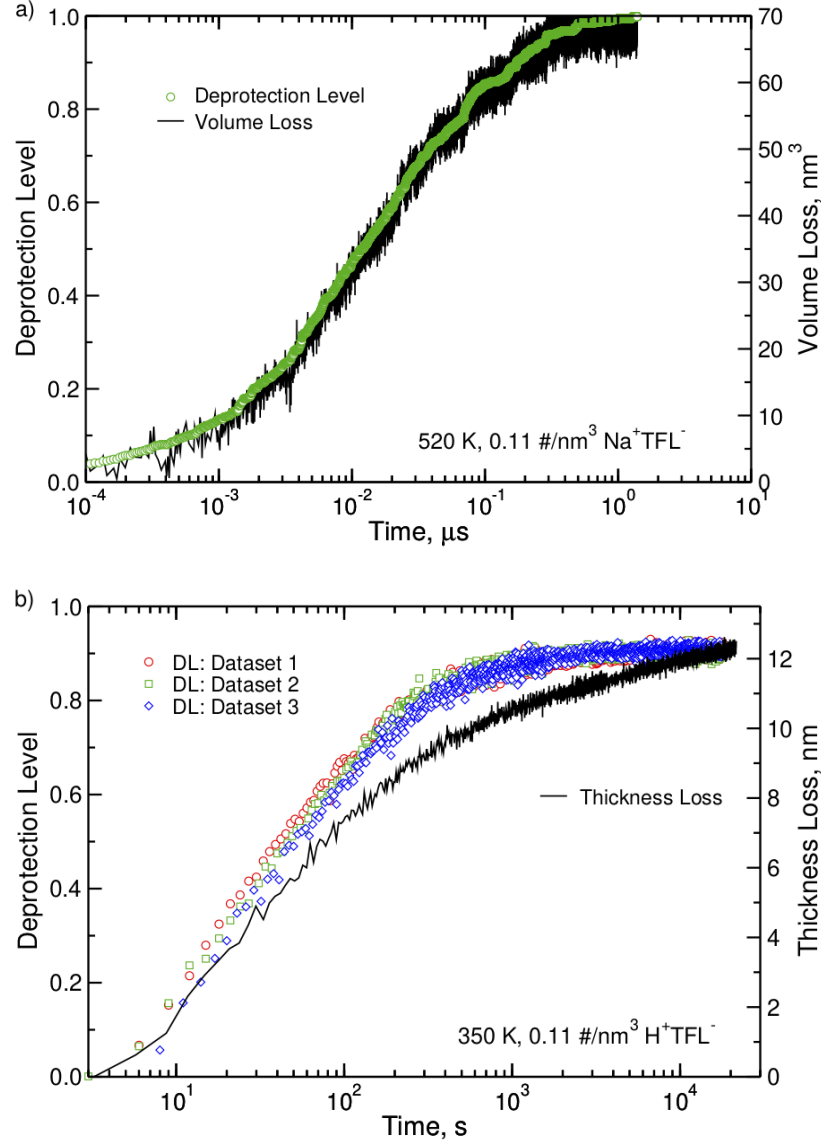


Figure 4.2: a) Deprotection level (symbols) and volume loss (line) for simulation with material relaxation at 520 K with 0.11 #/nm³ Na⁺TFL⁻. “Dataset” indicates replicate samples. b) Deprotection level (symbols) and thickness loss (line) obtained through FTIR and spectroscopic ellipsometry, respectively, for reacting thin film at 350 K with 0.11 #/nm³ H⁺TFL⁻.

4.2.3 Enhanced ion pair dynamics

The removal of protecting groups during simulations with material relaxation is expected to significantly impact ion pair dynamics. We aim to quantify the transient enhancement of ion pair dynamics to determine compare diffusion rates during reaction to those obtained in equilibrium simulations of the deprotected polymer. However, it is not a simple task to analyze the non-equilibrium dynamics introduced in this methodology. In these simulations, the local and global environments explored by ion pairs are continuously changing, therefore we chose to analyze ion pair dynamics by discretizing the simulation trajectory into equal log-spaced windows of time. This discretization allows us to extract the approximate ‘pseudo-steady states’ of ion pair dynamics where local environments experienced by ion pairs are not changing as significantly as they are in the overall simulation. As Na^+ cations do not dissociate from TFL^- counter-anions during these simulations, the dynamics of TFL^- COMs suffice to observe ion pair dynamics.

Figure 4.3a provides, for each time window, the $\text{MSD}/6t$ of TFL^- COMs for a simulation with material relaxation at 520 K with $0.11 \text{ \AA}^3/\text{nm}^3$ Na^+TFL^- . The inset provides the times and range of polymer composition present during each time window. These data show elevated ion pair dynamics at earlier time windows that decrease over simulation time towards the ion pair dynamics observed in equilibrium simulations of the deprotected polymer. Long-time plateaus in $\text{MSD}/6t$, observed in later time windows, correspond with Fickian dynamics and allow for the estimation of global TFL^- diffusivities. Early time windows are not sufficiently long to reach the Fickian regime. Therefore, TEKMC was applied to analyze these trajectories and model long-time dynamics. TEKMC provides a coarse-grained continuation of the TFL fluxes present in these short trajectories assuming no further changes in these local fluxes occur, and is described further in Section 4.1. These extended TFL^- dynamics allow for an estimation of the Fickian plateau for the determination of global TFL^- diffusivities. The extracted global diffusivities for each time window in this MD simulation with material relaxation are provided in Figure 4.3b. For global diffusivities, transition time refers to the time at the end of the analysis window. Global diffusivities

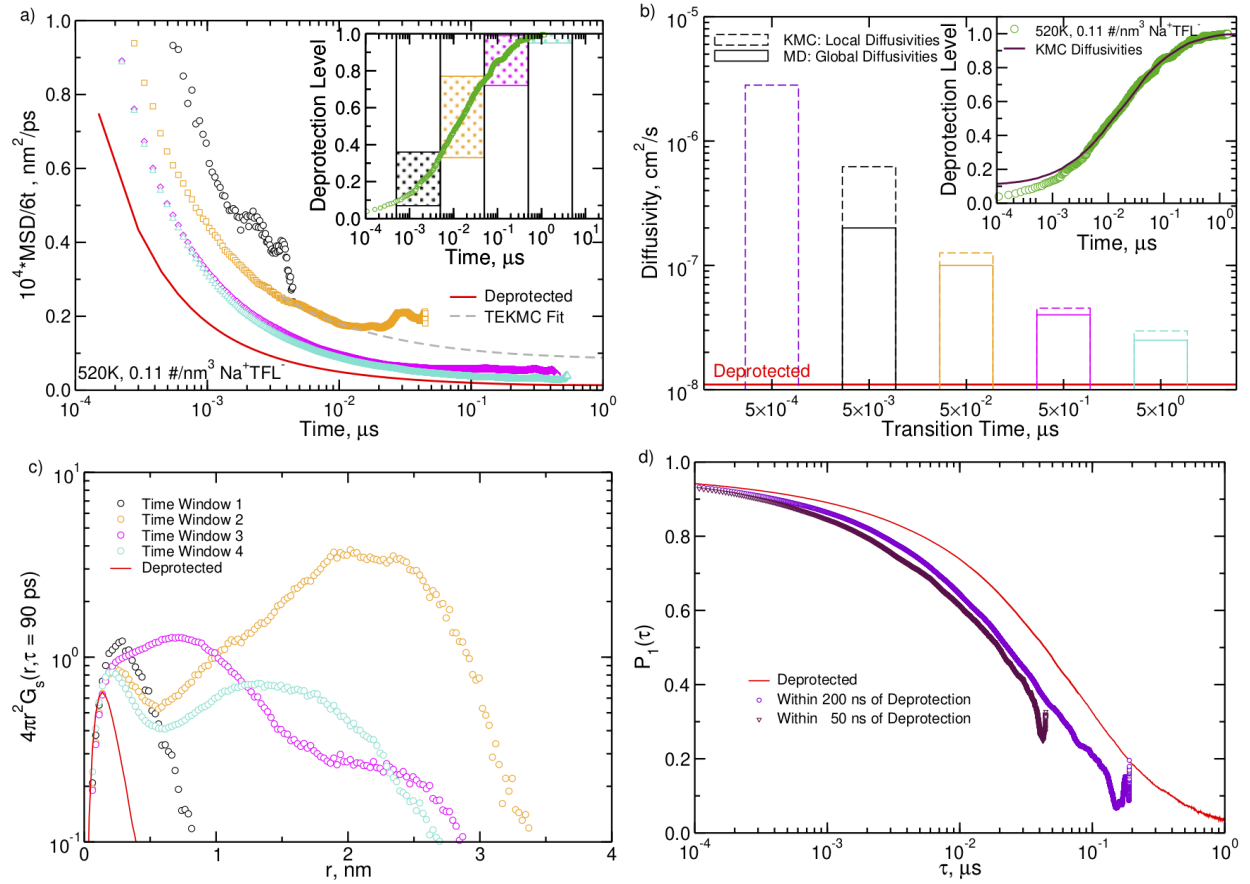


Figure 4.3: a) MSD/ $6t$ of TFL⁻ COMs. Data are obtained from time windows (colored symbols) in a simulation with material relaxation and from a simulation of the equilibrated deprotected polymer (line) at 520 K with 0.11 #/nm³ Na⁺TFL⁻. A representative TEKMC fit (gray dotted line) of the second time window is also shown. Time windows (corresponding colored boxes) are shown in the inset of deprotection level as a function of simulation time. b) Global (solid bars) and local (broken bars) diffusivities of TFL⁻s extracted from the simulation with material relaxation and a KMC model of the simulation's reaction kinetics as a function of transition time. The average diffusivity of TFL⁻s in the deprotected polymer (line) is also provided. Inset shows best-fit of KMC model (line) to reaction kinetics (symbols) of the simulation with material relaxation at 520 K with 0.11 #/nm³ Na⁺TFL⁻. c) Self-part of the van-Hove distribution of TFL⁻ COMs multiplied by $4\pi r^2$ in each analysis time window (symbols) and in the equilibrated deprotected polymer (line) for a timestep of 90 ps. d) Representative segmental dynamics of the polymer during the simulation with material relaxation. Dynamics are provided for HOST groups close (within 2 repeat units) to recently deprotected groups for the first 50 ns (triangles) and 200 ns (circles) after the deprotected groups are created. Segmental dynamics of HOST groups in the equilibrium deprotected polymer are also provided (line).

are observed to decrease over simulation time towards the TFL⁻ diffusivity observed in equilibrium simulations of the deprotected polymer.

To determine if global diffusivities could directly describe observed deprotection rates, a KMC model of a series of five elevated local diffusivities was developed. This model is described further in Chapter 5. The transition times for the conversion of one local diffusivity to the next were fixed to be the same as the times at the end of each analysis window. This limited the free parameters of the model to be five sequential diffusivities that relax to the diffusivities observed in the equilibrated deprotected polymer. An important distinction between this model and the analysis is that these transition times are relative to the time after the deprotection of a lattice site instead of the simulation time and that the diffusivities of the model describe local dynamics instead of the global diffusivity. The best-fit model of deprotection and corresponding local diffusivities are also provided in Figure 4.3b.

To accurately capture deprotection it was necessary to include an extra early-time diffusivity that occurs at shorter times than the first analysis time window. This indicates the presence of short-range and short-time diffusion at faster times than can be observed in our analysis of global diffusivities, but significantly contributes to deprotection and to the continued generation of transient states. We observe that local diffusivities at short transition times are significantly elevated when compared to global diffusivities. However, at long transition times the local diffusivities and global diffusivities begin to collapse together and decrease towards diffusivities in the equilibrium deprotected polymer.

To characterize the short-time enhancement in local diffusion rates in the simulation with material relaxation, the self-part of the van-Hove distribution ($G_s(r, \tau)$) of TFL⁻ COMs was determined at a timestep of 90 ps. This timestep was chosen to be an order of magnitude larger than reaction sampling but remains within the timescales of the fastest local diffusivity necessary to model reaction kinetics. Figure 4.3c provides $G_s(r, \tau)$ multiplied by $4\pi r^2$ for each time window of analysis and for TFL⁻ COM dynamics in the equilibrium deprotected polymer. The multi-modality observed in these data suggests heterogeneous TFL⁻ displacements during the simulation. The first peak indicates the motion of TFL⁻s

within local cages of approximately 0.7 nm radius and the development of a broad second peak in the second time window suggests that a build-up of recently reacted regions of the polymer generates pathways for TFL^- to escape these local cages. These distributions decrease and shift towards the distribution observed in the equilibrium simulation of the deprotected polymer over simulation time. This provides further evidence that the transient states generated by reaction are relaxing towards equilibrium over the course of the simulation as the densification of the polymer shrinks these local cages and increases the barrier to TFL^- diffusion.

The segmental dynamics of the polymer were characterized through the autocorrelation of the first Legendre polynomial ($P_1(\tau)$)[94] of the vector between the COM of the phenyl rings and the attached backbone carbon in HOSt repeat units, excluding end groups. HOSt groups were chosen for this analysis as they were previously found to interact strongly with the ion pairs in the equilibrium protected and deprotected polymers.[89] As segmental dynamics are spatially dependent in the simulations with material relaxation, these dynamics were analyzed for HOSt repeat units within two repeat units (approximately 0.75 nm) of recently deprotected groups on the same chain. These segmental dynamics are also time dependent, therefore the analyses were performed for a limited range of time after the deprotection of the recently deprotected group. Figure 4.3d provides the calculated segmental dynamics within 50 and 200 ns of a deprotection event in the simulation with material relaxation at 520 K with $0.11 \text{ \#}/\text{nm}^3 \text{ Na}^+\text{TFL}^-$. The total segmental dynamics of all HOSt groups within the equilibrium simulation of the deprotected polymer at 520 K with $0.11 \text{ \#}/\text{nm}^3 \text{ Na}^+\text{TFL}^-$ are also provided. Segmental dynamics with 50 ns of a deprotection event are observed to be over 5 times faster than the segmental dynamics observed at equilibrium. The slowing of segmental dynamics observed as the range of analysis time after a deprotection event is increased suggests that the enhancement in segmental is slowing over time towards the dynamics observed at equilibrium.

These methods provide evidence that ion pair diffusion is enhanced when you assume instantaneous byproduct escape, however they do not characterize what physical processes contribute to enhanced ion pair and polymer mobilities. Our prior work, and that of others,

suggests two important physical processes that may contribute to elevated ion pair dynamics:

- 1) The impact of the dispersion of ion pairs and related intermolecular interactions;[42, 89]
- and 2) The impact of free volume introduced through the removal of protecting groups.[10, 17, 19]

4.2.4 Effect of catalyst dispersion

In this section we aim to determine the impact of Na^+TFL^- concentration and dispersion on the simulations with material relaxation. In particular, how Na^+TFL^- dispersion impacts rates of reaction coupled to how material relaxation, including changes in composition, affects Na^+TFL^- dispersion. In our previous work, we found that Na^+TFL^- ion pairs exist in a balance between single ion pairs and low-order clusters in equilibrium simulations of the protected and deprotected polymer and the extent of clustering was impacted by polymer composition.[89] The presence of clusters decreased with decreasing temperature and Na^+TFL^- concentration, however we did not observe a significant impact of Na^+TFL^- concentration on TFL^- diffusivities in the absence of reaction. Since the reaction greatly impacts local diffusion rates in our simulations with material relaxation, it is expected that Na^+TFL^- dispersion will play a role in the observed acceleration of Na^+TFL^- diffusion.

We’ve determined that ion pair clustering has a significant impact on deprotection rates in these simulations with material relaxation. This is demonstrated by the characterization of the average cluster size of TFL molecules. The average cluster size is determined through the number of TFL^- COMs within a 0.75 nm radius of a reference TFL^- ’s COM, inclusive of the reference. An average cluster size of 1 corresponds to an individual ion pair while 2 corresponds with a dimer of ion pairs and 3 corresponds to a trimer. Figure 4.4a provides deprotection data and the average cluster size for three simulations with material relaxation: 1) 520 K with 0.11 #/nm³ Na^+TFL^- starting from a configuration of randomly dispersed ion pairs in the protected polymer; 2) 520 K with 0.11 #/nm³ Na^+TFL^- starting from a configuration of equilibrium clustered ion pairs in the protected polymer obtained from the final configuration of previous equilibrium simulations; and 3) 520 K with 0.05 #/nm³

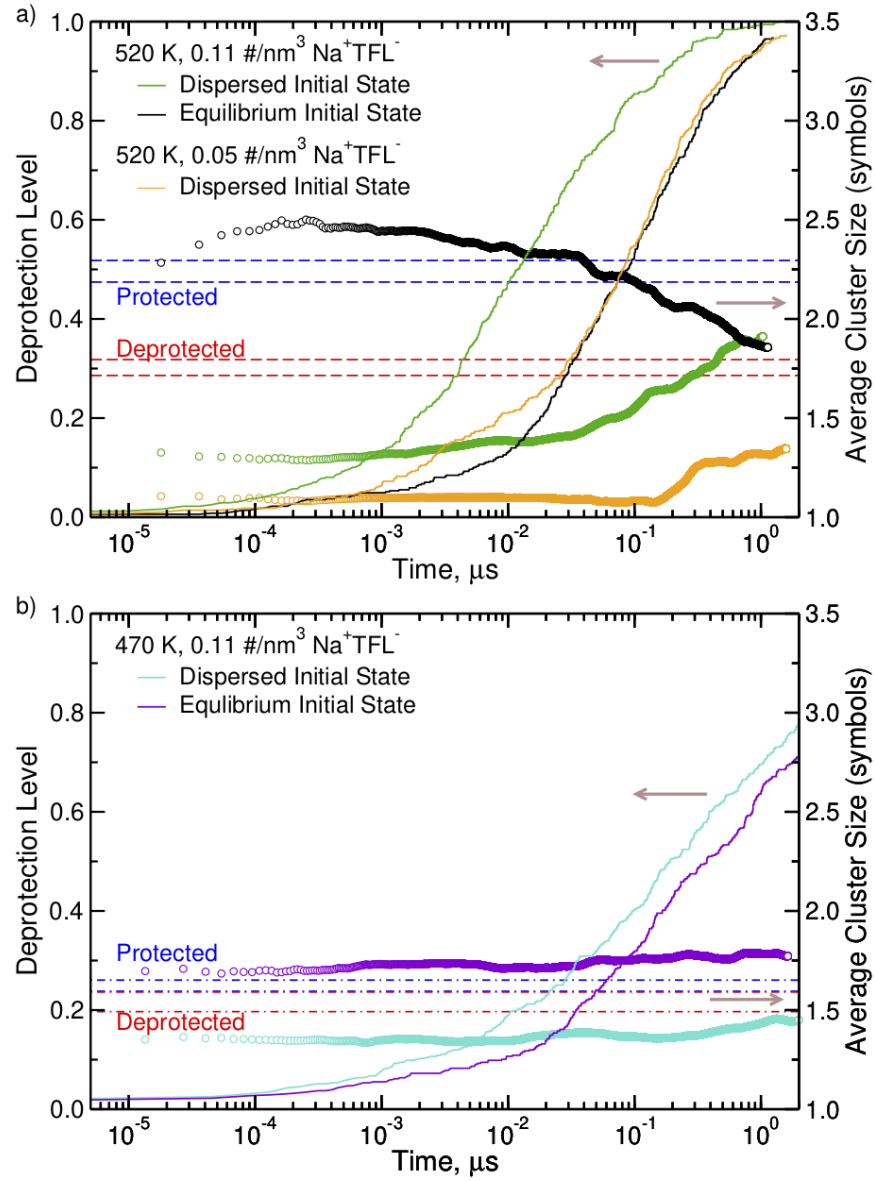


Figure 4.4: a) Deprotection level and average size of TFL⁻ clusters for simulation with material relaxation at 520 K with 0.11 #/nm³ Na⁺TFL⁻ starting from either an initially dispersed or initially clustered equilibrium state and with 0.11 #/nm³ Na⁺TFL⁻ starting from an initially dispersed state. b) Deprotection level and average size of TFL⁻ clusters for simulation with material relaxation at 470 K with 0.11 #/nm³ Na⁺TFL⁻ starting from either an initially dispersed or initially clustered equilibrium state. In both figures, horizontal dotted lines indicate a 95% confidence interval of the equilibrium average cluster size observed for 0.11 #/nm³ Na⁺TFL⁻ in the protected and deprotected polymers at the respective temperatures.

Na^+TFL^- starting from a configuration of randomly dispersed ion pairs. These data show that when ion pairs are initially clustered deprotection occurs at significantly reduced rates compared to the dispersed initial state. This reduction is likely the result of clusters promoting similar deprotection as that of single ion pairs as they access similar material volumes. This is further evidenced by the similarity between deprotection rates of the cluster system and deprotection rates observed at reduced Na^+TFL^- concentration.

Figure 4.4b provides data for simulations with material relaxation at 470 K with $0.11 \text{ \AA}^3$ Na^+TFL^- in either the initially dispersed or the equilibrium clustered state. These data show that at lower temperatures the differences in deprotection rates are reduced, likely due to the significant reduction in average cluster size. These results suggest that catalyst clustering could reduce the effective concentration dependence of reaction and, consistent with our prior results in the absence of reaction,[89] that this reduction should decrease with decreasing temperature. It is likely that catalyst dispersion plays an important role in controlling reaction and diffusion at experimental temperatures, as catalyst clustering could reduce the apparent catalyst loading, but reduced clustering at lower temperatures suggests that it is unlikely to be the sole contribution to predicted transient diffusion states.

4.2.5 Excess free volume generation

The removal of protecting groups introduces pockets of unoccupied volume that must equilibrate over the course of our simulations with material relaxation. These pockets introduce heterogeneities in local density within the polymer matrix and are expected to contribute to the observed acceleration of short-range TFL^- dynamics as well as impact the local dynamics of the polymer. This section aims to quantify this introduced free volume and compare the timescales of generation and relaxation of this free volume to the timescales of enhanced diffusivities.

The global free volume of a simulation cell can be estimated through random insertions of small spherical probes.[95] By rejecting probe insertions that overlap with spheres of half the van der Waals radii of simulated atoms, we can estimate the free volume of the system

by multiplying the ratio of accepted insertions to attempted insertions by the volume of the simulation cell. A slightly larger than typical probe size of 3 Å was chosen to weight the estimate towards pockets of free volume large enough for ion pairs to diffuse through. To determine if the removal of protecting groups produces excess free volume (EFV), or free volume that is not present at equilibrium, the free volume as a function of polymer composition at equilibrium must first be determined. Configurations at a series of polymer compositions were obtained from the simulation with material relaxation and allowed to equilibrate prior to free volume analysis. Figure 4.5a provides the free volume of a simulation with material relaxation at 520 K with 0.11 #/nm³ Na⁺TFL⁻ and the estimated equilibrium free volume as a function of simulation time. The estimated equilibrium free volume is calculated from deprotection level using the polynomial calibration curve, provided in the inset, that describes the free volume of the equilibrated series of polymer compositions. These configurations were obtained by picking configurations of a specific composition from this simulation with material relaxation and allowing for the material to fully equilibrate through 100 ns NPT simulations. The free volume analysis of the simulation is inherently noisy as only one configuration is analyzed at each time, however the 10-point running average of free volume shows that free volume during the simulation with material relaxation is elevated above the equilibrium estimate for most of the simulation.

By subtracting the equilibrium estimate from the 10-point running average and dividing the result by the equilibrium estimate we obtain the fractional excess free volume (FEFV). Figure 4.5b provides a comparison between FEFV and deprotection as a function of temperature and Na⁺TFL⁻ concentration. For the simulation with material relaxation at 520 K with 0.11 #/nm³ Na⁺TFL⁻ we observe that FEFV is generated at the onset of deprotection (0.2 ns), builds up during periods of high deprotection and diffusion rates (0.2 - 50 ns), and is depleted as the material relaxes (>50 ns). As shown in Figure 4.3b, elevation in global diffusivities persist past 50 ns, however they are only 2 times the equilibrium deprotected diffusivity at these timescales as opposed to the more than 1 order of magnitude enhancement prior to 50 ns. FEFV at 520 K with 0.11 #/nm³ Na⁺TFL⁻ is shown to be increased relative to FEFV at 0.05 #/nm³ Na⁺TFL⁻, corresponding with

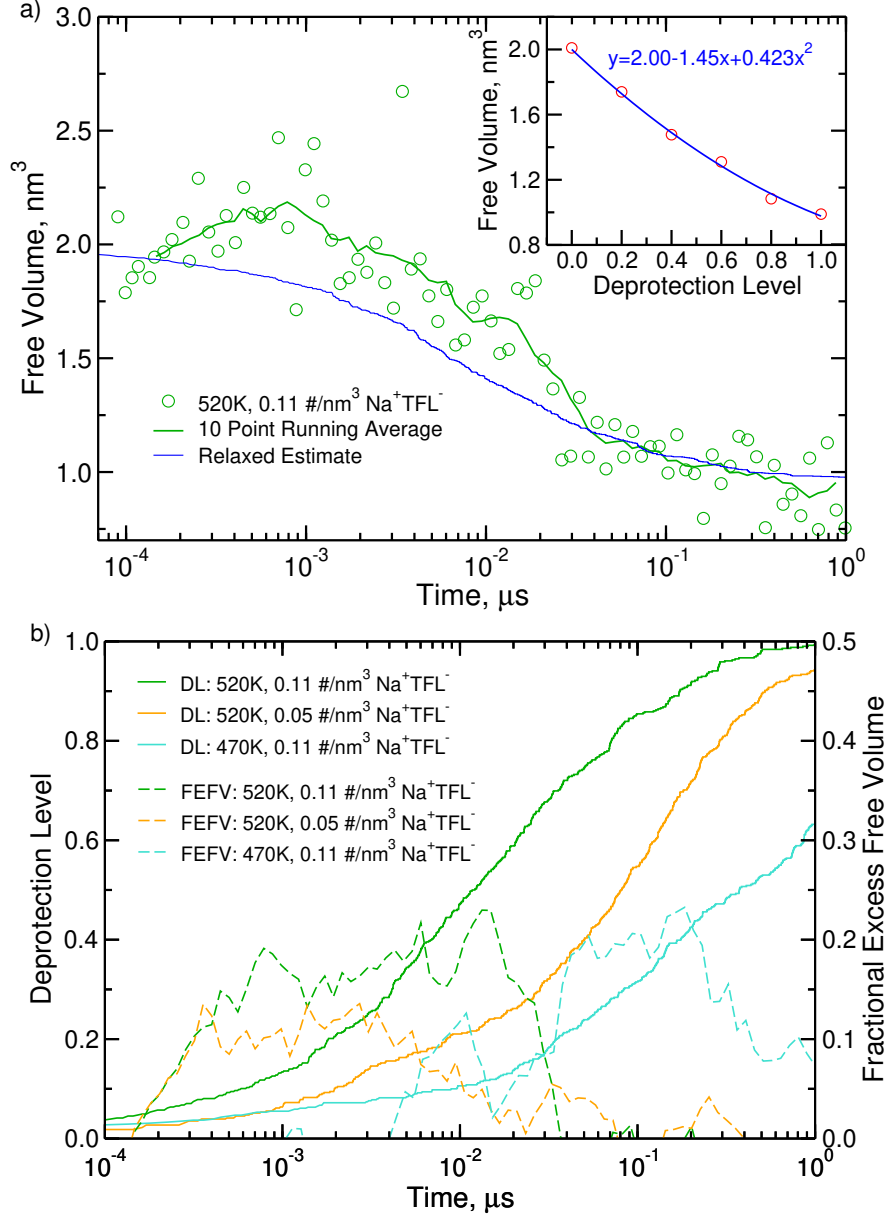


Figure 4.5: a) Free volume calculated from $3 \text{ \AA}$ radius spherical probe insertions for simulation with material relaxation at 520 K with $0.11 \text{ \#}/\text{nm}^3 \text{ Na}^+\text{TFL}^-$ along with the running average of 10 point bins. An estimate of the composition-dependent equilibrated free volume is also provided. Inset provides the polynomial calibration curve of free volume vs deprotection level. This calibration curve is fit to equilibrated free volumes obtained from 100 ns NPT simulations with initial configurations selected from this simulation with material relaxation. b) Deprotection level and fractional excess free volume for simulations with material relaxation at 520 K with 0.11 and $0.05 \text{ \#}/\text{nm}^3 \text{ Na}^+\text{TFL}^-$ and at 470 K with $0.11 \text{ \#}/\text{nm}^3 \text{ Na}^+\text{TFL}^-$.

increased deprotection rates at higher Na^+TFL^- concentrations. The lower deprotection and diffusion rates at 470 K delay the onset of FEFV and slower rates of polymer relaxation at this temperature prolong its presence. These results persist at all conditions analyzed for simulations with material relaxation.

Prior literature suggests that the presence of free volume in polymers can significantly increase the dynamics of the polymer as well as the dynamics of penetrants.[95,96] In melts and glasses, penetrants diffuse to new areas of the polymer by moving through pockets of accessible volume between the polymer chains.[31] The distribution of this accessible volume rearranges as the polymer moves and the introduction of excess free volume should increase the size and connectivity of these pockets, which in turn increases penetrant diffusion. Croffie et al theorized and modeled the elevation of catalyst diffusion and reaction due to excess free volume in CARs through a modified version of the Fujita-Doolittle equation,[19] which is commonly used to model viscosity as a function of free volume. This equation is described further in Chapter 6 (Equation 6.1). Using this equation, and reasonable parameters at this temperature for non-interacting penetrant diffusion ($\omega = 10$, $\nu = 1$, $D_0 = 1 \times 10^{-7} \text{ cm}^2/\text{s}$),[15, 19, 97] we estimate that a FEFV of 20% could result in over a two order of magnitude increase in penetrant diffusivity when compared to the diffusivity in the absence of reaction. A more recent molecular dynamics study of penetrant diffusion in polyvinyl chloride copolymers, which determined accessible free volume through 2 Å probe insertions, found that an approximate 3% increase in fractional accessible free volume increased N_2 diffusivities by 1 order of magnitude.[95] The elevation of penetrant diffusivities due to elevated free volume in these studies are consistent with the elevation in diffusivities observed in our simulations with material relaxation, which lends support to excess free volume playing a major role in the enhancement of ion pair and polymer dynamics.

4.3 Conclusions

We presented a molecular dynamics study of enhanced catalyst mobility during reaction produced by transient materials states introduced through the removal of protecting groups.

These simulations provide detailed data on the competition between coupled reaction-diffusion and material relaxation. Local Na^+TFL^- diffusivities were found to be transiently elevated over two orders of magnitude higher than diffusivities in the equilibrium deprotected polymer. At 520 K, these diffusivities were found to fully relax to the equilibrium state over the course of multi- μs simulations. Analysis of the distribution of short-time diffusion lengths through the van-Hove distributions suggest ion pairs exist at equilibrium in cages of approximate 0.7 nm and that the removal of protecting groups generates pathways for ion pairs to escape these cages. Catalyst dispersion was found to contribute to the rates of reaction as clustered ion pairs are observed to promote reaction in a similar manner to single ion pairs, reducing the overall ion pair concentration dependence of reaction rates. The excess free volume generated by removal of protecting groups was quantified as a function of temperature and ion pair concentration. The two orders-of-magnitude enhancement in local diffusivities is found to be consistent with literature estimations of the impact of increased free volume on penetrant diffusivities. This suggests that excess free volume plays an important role in the acceleration of catalyst diffusivities observed in experiments.

Chapter 5

Kinetic Monte Carlo model of transient local diffusivities

The simulations with material relaxation allowed us to determine the impacts of protecting group removal on catalyst diffusion and the related aspects of catalyst dispersion, excess free volume generation, and material densification. These results guide the development of a mesoscale model of transiently accelerated local diffusivities that can capture observed reaction kinetics in both simulations ($T \gg T_g$) and experiments ($T < T_g$).

5.1 Methods

5.1.1 Mesoscopic models

Multi-diffusivity kinetic Monte Carlo. A lattice model of catalyst diffusion was developed in a similar manner to prior work in the Stein and Doxastakis groups.^[45] The prior model, that utilized a single Fickian catalyst diffusivity, was unable to describe reaction kinetics. This was attributed to the predicted transient nature of catalyst diffusion that the

Author notes: Parts of this chapter are adapted from C. M. Bottoms, G. E. Stein, and M. Doxastakis, “Transient diffusion states during reaction in chemically amplified resists,” 2022 Manuscript submitted for publication in special issue of Journal of Physical Chemistry A.

model did not capture. However, this new model assumes that catalysts progress through states of elevated local diffusivities before relaxing to the slow diffusivities observed in the absence of reaction.[89] For the model, the lattice is divided into cubic sites of 1 nm^3 (d^3) volume and catalysts are placed randomly within the lattice framework according to the required $\#/\text{nm}^3$ initial concentration. Events are modeled using a stochastic kinetic Monte Carlo (KMC) approach,[98, 99] where reactions, hopping, and transitions are implemented based on the combination of exponential distributions of time intervals associated with individual events:

$$\Psi(t) = \frac{1}{\tau} e^{-t/\tau} \quad (5.1)$$

Lattice sites are initially considered protected, with a site-dependent catalyst diffusivity corresponding to diffusion in the absence of reaction (D_0).[89] Catalysts immediately react their initial positions and instantaneously deprotect any protected site visited at subsequent times. When a site becomes deprotected, the site-dependent catalyst diffusivity is initially elevated to the maximum diffusivity (D_n) of the model, where n is the number of elevated diffusivities. The catalyst diffusivity of this site, independent of catalyst occupancy, progresses through a series of lowered diffusivities with independent transition rates (k_n) until the site returns to D_0 . Catalyst hopping events are selected from jumps to the 6 nearest neighbors where jump rates are calculated from the average diffusivity of the origin and destination site. Figure 5.1 is a graphical 2 dimensional representation of the modeled reaction and diffusion. The implementation of this model of transient local diffusion states creates a broad and time-dependent distribution of local diffusivities. The average of all site-dependent catalyst diffusivities increases with the quick generation of deprotected sites but relaxes over time to D_0 . A version of the model with five elevated diffusivities with fixed transition rates is used to extract local diffusivities and compare them to global diffusivities in simulations with material relaxation in Chapter 4. A model with the four free parameters being two elevated diffusivities and the two corresponding transition rates is used in this chapter to model deprotection in simulations with material relaxation and to model experimental reaction kinetics.

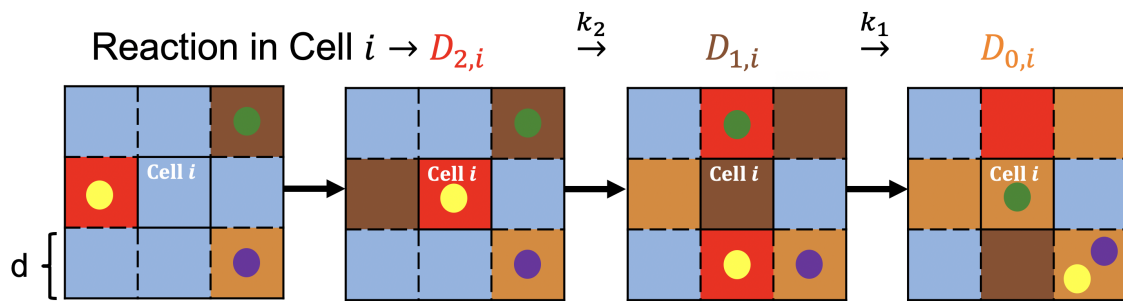


Figure 5.1: Schematic of the development of local diffusivities, reaction, and catalyst probe hopping in the KMC model.

5.2 Results

5.2.1 Modeling of simulations with material relaxation

This study aims to develop a model of reaction kinetics that is informed by the physics observed in our simulations of material relaxation. The multi-diffusivity KMC model with fixed transition rates, introduced earlier (Chapter 4) to estimate local diffusion rates, can describe the deprotection of all simulations with material relaxation by optimization of the modeled diffusivities. However, the numerous parameters in the model make it difficult to directly compare diffusivities across a range of temperatures, as the important timescales of reaction kinetics shift significantly. Therefore, we developed a simplified four parameter KMC model that captures transient local diffusion states through a series of elevated diffusivities, D_2 and D_1 in Figure 5.1. The accelerated diffusivity, D_2 , produced by the reaction relaxes to the diffusion in the inert state, D_0 , through an intermediate diffusivity, D_1 . D_2 and D_1 , and transition rates between diffusivities of k_2 and k_1 , were adjustable parameters for optimization. D_0 in the model was fixed to the diffusivity of Na^+TFL^- in the deprotected polymer, determined in our previous work.[89] As shown in Figure 5.2a, the model captures observed deprotection from our simulations with material relaxation at 520, 470, and 420 K with $0.11 \text{ \#}/\text{nm}^3 \text{ Na}^+\text{TFL}^-$.

The optimized model parameters follow an Arrhenius temperature dependence, as shown in Figure 5.2b. The trends on the log-inverse plot have similar slopes, except for the transition rate to the equilibrium diffusivity, k_1 , which displays a significantly reduced activation energy for relaxation to the equilibrium diffusivity. As shown in Appendix A (Figure A.10), the optimized diffusivities at 520 K for lower Na^+TFL^- concentrations ($0.05 \text{ \#}/\text{nm}^3$) and for equilibrium clustered initial states are similar to diffusivities at $0.11 \text{ \#}/\text{nm}^3$. As previously shown in Figure 4.4a, the deprotection level in simulations at 520 K that start from the equilibrium clustered state closely matches that observed at $0.05 \text{ \#}/\text{nm}^3 \text{ Na}^+\text{TFL}^-$. This results in the optimized diffusivities and transition rates being similar, which suggests that clustering may effectively reduce the Na^+TFL^- concentration dependence of the optimized

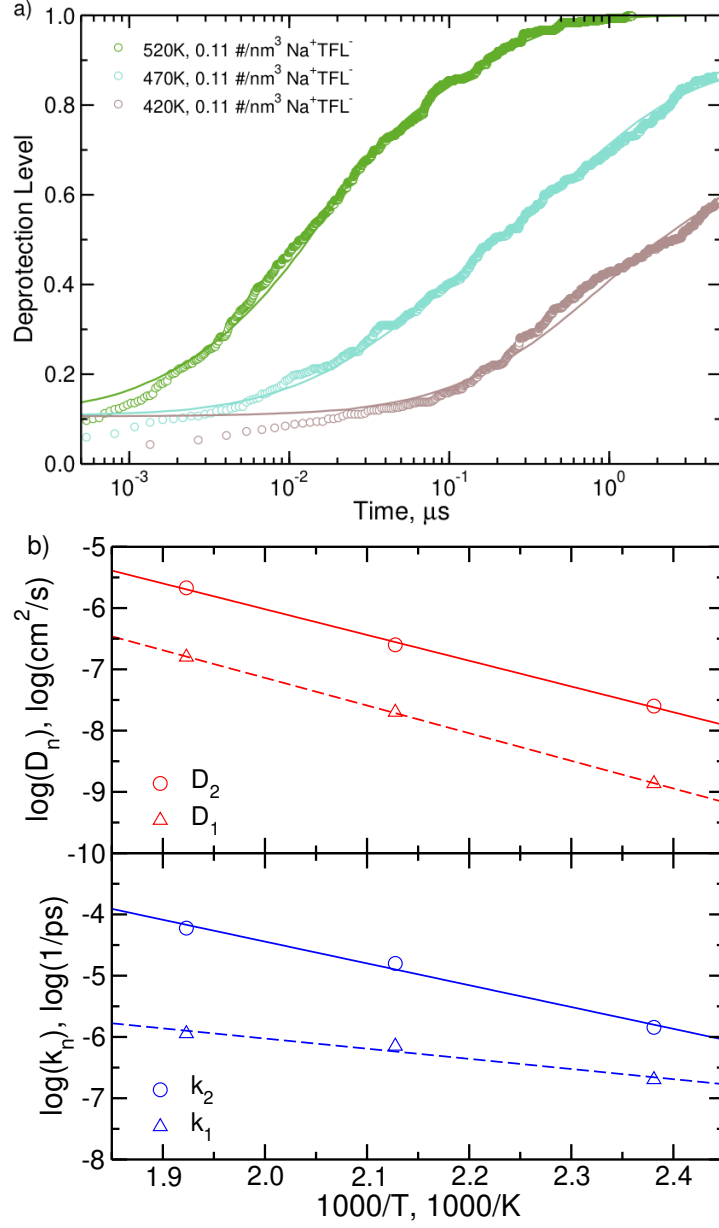


Figure 5.2: a) Deprotection level (symbols) for simulations with material relaxation at 520 K, 470 K, and 420 K with $0.11 \text{ \#}/\text{nm}^3 \text{ Na}^+\text{TFL}^-$. Best-fit KMC models of transient diffusivities (lines) are provided. b) Temperature dependence of model parameters (symbols) are provided along with best-fit Arrhenius models (lines).

parameters. The transition rates are slightly reduced in the lower Na^+TFL^- concentration compared to the highest Na^+TFL^- concentration at 520 K. We attribute the slower transition rate to be the result of an observed decrease in the equilibrium simulation density at lower concentrations of the Na^+TFL^- , which lowers the driving force for relaxation.

5.2.2 Modeling of experiments

The simplified KMC model of two elevated local diffusion states also describes experimental reaction kinetics at a variety of catalyst concentrations for temperatures below T_g . Thin films of the protected terpolymer containing active catalyst were prepared as described in Section 5.1 and reaction kinetics was monitored using FTIR. The model provides good agreement in a catalyst concentration range of 0.05 to 0.11 $\#/\text{nm}^3$ H^+TFL^- and in the temperature range of 335 to 350 K. However, the same model parameters cannot describe reaction kinetics across all concentrations if we assume that the catalysts are fully dispersed (average cluster size of 1), as shown in Appendix A in Figure A.11.

Since simulations suggest that catalyst dispersion plays an important role in describing reaction kinetics, we introduce a new parameter denoted as the cluster size factor, α , that reduces the effective catalyst concentration ($[\text{H}^+\text{TFL}^-]_{\text{eff}}$) of the model. This reduction is assumed to be induced by catalyst clustering and introduced by dividing the experimental concentration by the clustering factor (ξ):

$$[\text{H}^+\text{TFL}^-]_{\text{eff}} = [\text{H}^+\text{TFL}^-]/\xi \quad \text{where} \quad \xi = 1 + \frac{(\alpha - 1)([\text{H}^+\text{TFL}^-] - 0.05)}{(0.11 - 0.05)} \quad (5.2)$$

where α is an adjustable fitting parameter that relates to catalyst clustering at a catalyst concentration of 0.11 $\#/\text{nm}^3$. By assuming that clusters behave similar to single catalysts, α is an estimate of the average cluster size at a catalyst concentration of 0.11 $\#/\text{nm}^3$ H^+TFL^- . This equation assumes no clustering is present at 0.05 $\#/\text{nm}^3$ and that clustering between 0.05 and 0.11 $\#/\text{nm}^3$ is linearly dependent on catalyst concentration. Equation 5.2 describes the impact of α on the effective catalyst concentration in the model under the assumption that catalyst clusters do not change significantly during reaction.

As shown in Figure 5.3a, the introduction of this effective catalyst concentration allows the model to closely describe experimental reaction kinetics across all concentrations. We attribute these early time deviations to nonisothermal effects, as it takes approximately 20 sec at 350 K for the sample to reach the set temperature of the heat cell. The α of 1.37 at 350 K implies that low-order clustering is present for the highest catalyst concentrations, with estimated cluster sizes of 1.19 and 1.00 for 0.08 and 0.05 $\#/\text{nm}^3$ H^+TFL^- , respectively. However, the inset of Figure 5.3b shows that α decreases with decreasing temperature, which is consistent with our prior work.[89] This result is also consistent with the decreased clustering of TFL $^-$ -based ion pairs with decreasing temperature observed in polymer electrolytes.[100, 101] The temperature dependence of the optimized model parameters follow an Arrhenius model, as shown in Figure 5.3b, with similar activation energies (slopes) except for a slight increased temperature dependence of D_1 . This suggests that as temperature decreases, the difference between D_2 and D_1 increases which broadens the predicted reaction kinetics curves.

5.3 Conclusions

We developed a KMC model of transient local diffusion states, informed by the results of our simulations, that is found to describe reaction kinetics in both simulations (above T_g) and experiments (below T_g). The model can describe experimental reaction kinetics across all catalyst concentrations by accounting for low amounts of catalyst clustering. This model creates an important bridge between the atomistic detail provided by simulations and measurements of reaction kinetics from FTIR.

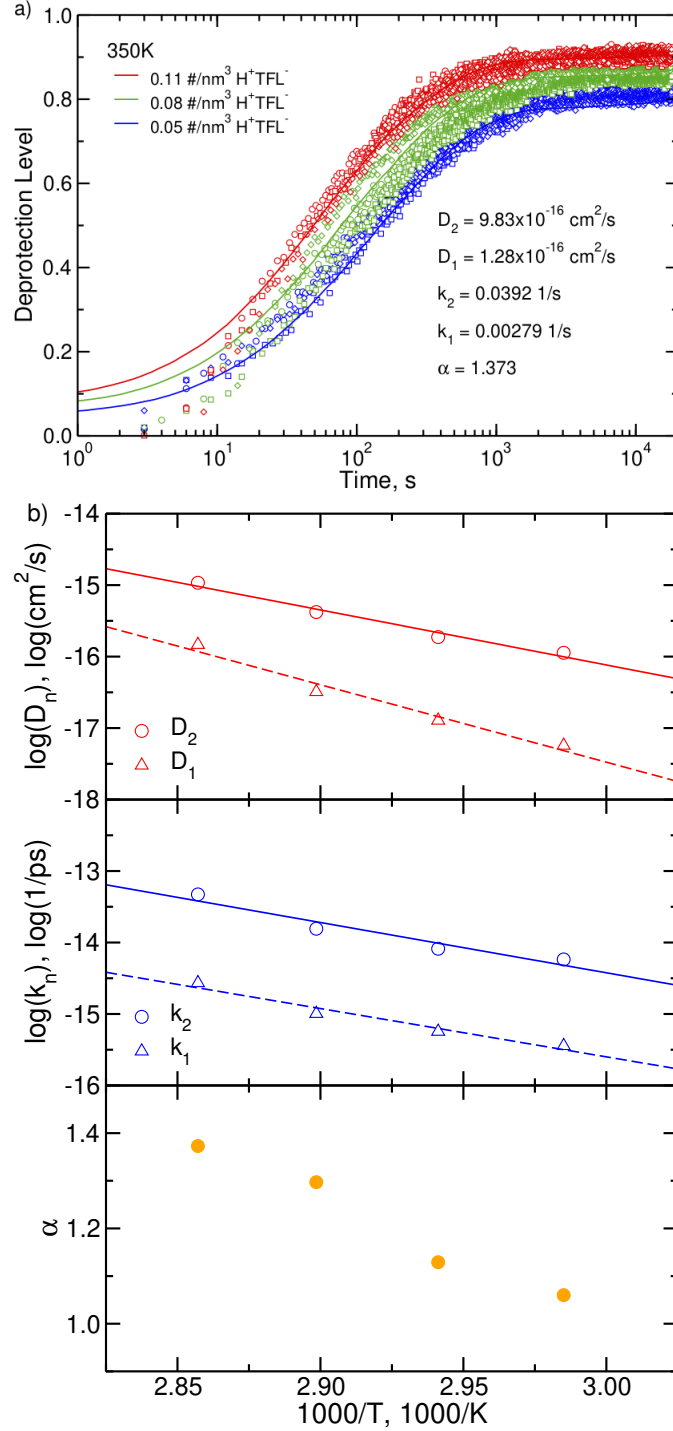


Figure 5.3: a) Deprotection level (symbols) for experimental reaction kinetics at 350 K with 0.11, 0.08, and 0.05 $\text{\#}/\text{nm}^3$ H^+TFL^- . Best-fit KMC model of transient diffusivities (lines) are provided using the same model parameters. Best-fit cluster size factor (α), used to describe concentration dependence of the model, and other model parameters are provided. b) Temperature dependence of model parameters (symbols) are provided along with best-fit Arrhenius models (lines). Inset provides the temperature dependence of α .

Chapter 6

Applications of KMC model of transient diffusivities

In this section, we employ the KMC model of transient local diffusivities to probe aspects of the CAR system that are difficult to measure experimentally. The model serves as a bridge between the bulk reaction kinetics experiments and the physical processes that are controlling catalyst diffusion at the molecular level. This allows for the determination of the effect of counter-anion size on catalyst diffusion and clustering. This also allows for estimates of the excess free volume that produces the locally-enhanced diffusivities in the model, which can then be compared with measurements of film thickness relaxation. This comparison, along with mass spectrometry analysis of volatilized reaction byproducts, provides evidence that generation of excess free volume and accumulation of byproducts could both contribute to accelerated catalyst diffusion during reaction.

6.1 Methods

6.1.1 Experiments

Deprotection Reaction. Thin films of triphenylsulfonium perfluorobutanesulfonate (TPS-PFBS) in the protected polymer were created in similar manner to the priorly reported

method with TPS-TFL.[89] Solutions for casting films were prepared with 8 wt% protected polymer in PGMEA and 4.1, 6.8, and 9.5 wt% TPS-PFBS with respect to the polymer. Films were spin-coated from these solutions onto double-side polished silicon wafers at 2000 rpm. Residual solvent was removed by baking films at 403 K for 4 mins. Resulting films contain 0.05, 0.08, and 0.11 #/nm³ TPS-PFBS with thicknesses of approximately 250 nm. Films are exposed to UV-light, as previously described, to fully convert all TPS-PFBS to the active catalyst H⁺PFBS⁻ with some assumed production of photoactivation byproducts. Reaction kinetics for these films at 335, 340, 345, and 350 K were gathered using FTIR Spectroscopy following the previously described method. Reaction kinetics for films of the protected polymer with H⁺TFL⁻ were the same as those described earlier, Chapter 2.

Film Thickness. Thin films of 0.05, 0.08, and 0.11 #/nm³ H⁺TFL⁻ in the protected polymer were created in the same manner as the films for previously described reaction kinetics measurements. The same spectroscopic ellipsometer and polarization model described in Chapter 3 were used to measure the ellipsometry parameters and extract film thickness as a function of thermal annealing time at 340 K using an in-situ heat cell.

Thermogravimetric Analysis - Mass Spectrometry (TGA-MS). A film of 0.11 #/nm³ TPS-TFL in the protected polymer was drop cast onto an uncoated sheet of Mylar from a solution of 8 wt% protected polymer in PGMEA and 7 wt% TPS-TFL with respect to the polymer. The film on Mylar was baked at 403 K for 5 mins to remove residual solvent. The film was exposed to UV-light, as previously described, to activate the H⁺TFL⁻ catalyst and was peeled from the Mylar as a free-standing film. TGA-MS using a TA Discovery TGA-MS analyzer was performed on the resulting film using a platinum sample pan. The sample chamber was preheated to 343 K, then the sample was loaded into the chamber and data acquisition immediately initiated upon closure of the chamber. The sample was held at 343 K for 1800s, linearly raised to 393 K over the course of 1000 s, and held at 393 K for 900 s. The weight % and mass spectra were recorded concurrently throughout the experiment.

Mass/charge (m/z) ratios of 56, indicative of the reaction byproduct 2-methylpropene, and 72, indicative of residual PGMEA solvent, were analyzed.

6.2 Results

6.2.1 Effect of counter-anion size

This section uses the KMC model to probe the effects of increased counter-anion size on local diffusivities and catalyst clustering. A prior study that compared H^+TFL^- with H^+PFBS^- , a catalyst with a larger counter-anion, measured a decrease in reaction kinetics with increasing counter-anion size.[21] This study suggested that increased counter-anion size decreased the diffusivities of the catalyst. However, another study of the same two catalysts that measured the spatial extent of reaction fronts suggested that catalyst diffusivities were the same.[27] The TFL^- anion has an approximate diameter of 4.6 Å (estimated using the van der Waals radii of the atoms) while the PFBS^- anion has an approximate diameter of 7.4 Å. In polymer glasses, penetrants that weakly interact with the polymer diffuse more slowly as their size increases.[102,103] In our CAR system the catalyst strongly interacts with both the polymer and with other catalysts,[89] which significantly complicates penetrant diffusion.[104,105]

Films of the CAR resist with TPS-PFBS photoacid generator were prepared as described in Chapter 3, and reaction kinetics was measured with in-situ FTIR as described in Chapter 2. Figure 6.1 shows reaction kinetics data for both H^+TFL^- and H^+PFBS^- at 340 K and catalyst loadings of 0.05, 0.08, and 0.11 #/nm³. Reaction rates and long-time deprotection levels are reduced for H^+PFBS^- when compared to H^+TFL^- . The KMC model captures reaction kinetics for all catalyst concentrations at each temperature studied.

Figure 6.2 reports the optimized model parameters for both systems as a function of reaction temperature. Local diffusivities are similar in both systems while transition rates are slightly elevated in H^+PFBS^- over H^+TFL^- . This suggests that local diffusion rates during reaction are similar, but accelerated local diffusivities approach equilibrium faster with H^+PFBS^- than with H^+TFL^- . This result is consistent with the decreased hydrophilicity

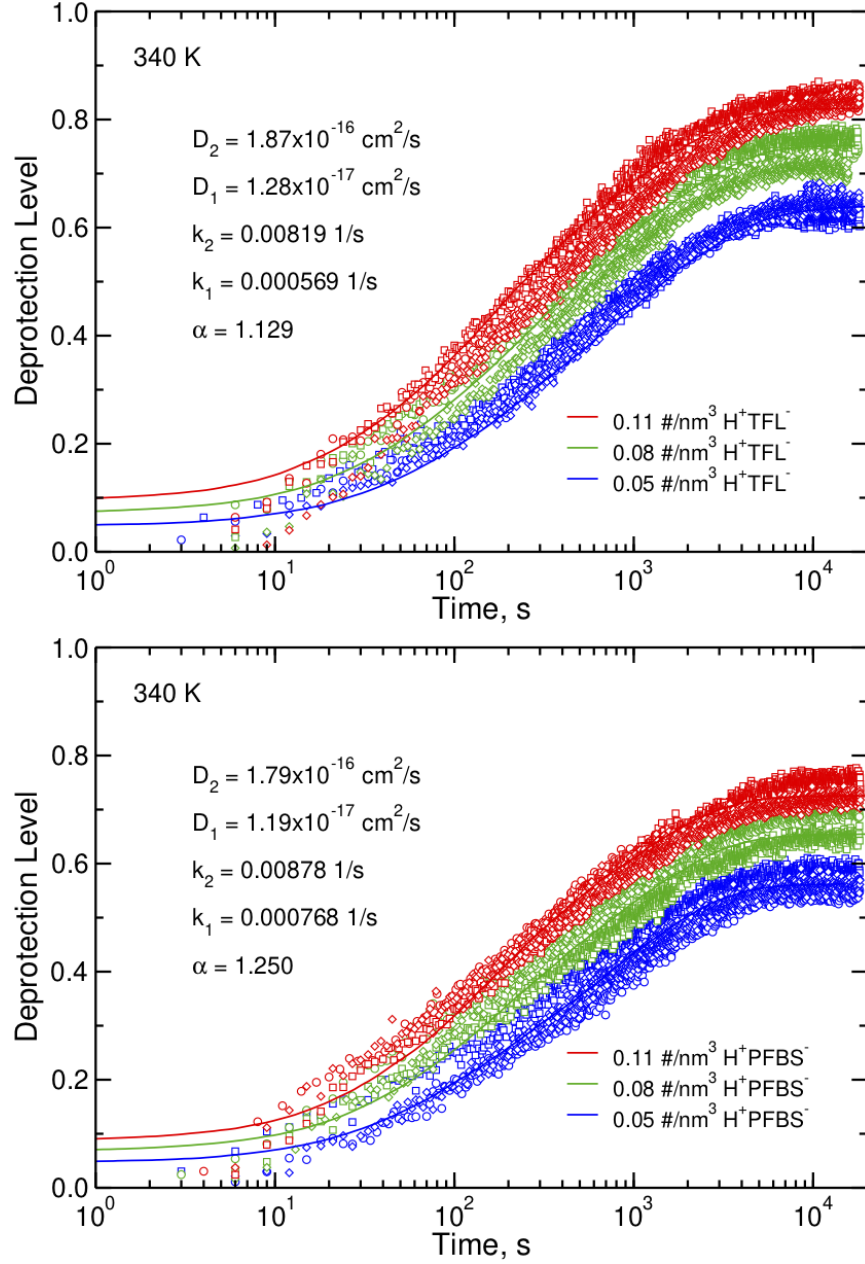


Figure 6.1: a) Deprotection level (symbols) for experimental reaction kinetics at 340 K with 0.11, 0.08, and 0.05 $\#/\text{nm}^3$ H^+TFL^- . Best-fit KMC model of transient diffusivities (lines) are provided using the same model parameters. Best-fit cluster size factor (α), used to describe concentration dependence of the model, and other model parameters are provided. b) The same for H^+PFBS^- .

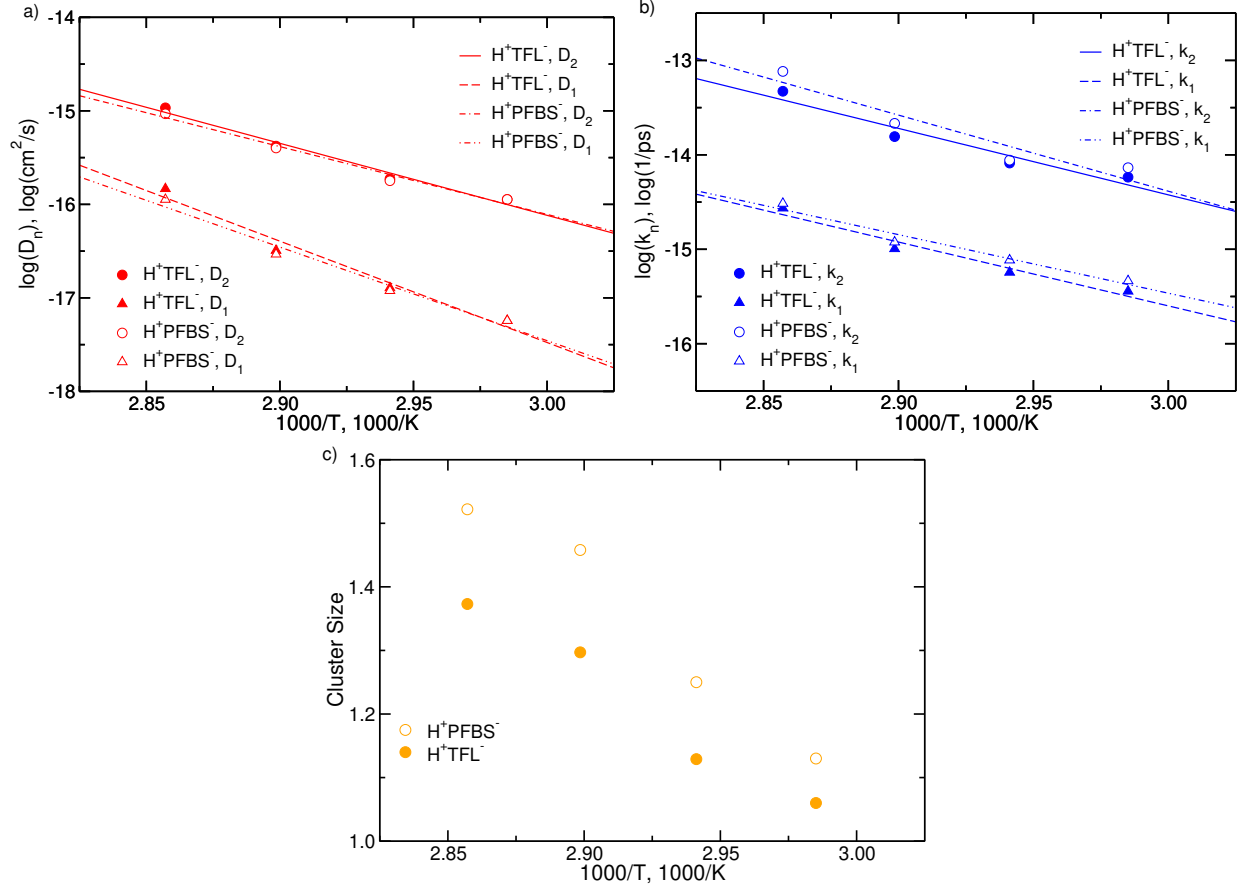


Figure 6.2: a) Temperature dependence of model diffusivities of H^+TFL^- (filled symbols) and H^+PFBS^- (empty symbols) are provided along with best-fit Arrhenius models (lines). b) Temperature dependence of model transition rates of each system along with best-fit Arrhenius models (lines). c) Temperature dependence of the α in each system.

of H^+PFBS^- , compared to H^+TFL^- ,^[106] which decreases hydrogen bonding within the polymer. This could decrease the density of the polymer and quicken segmental dynamics, promoting the relaxation of accelerated diffusivities. In support of this claim, Figure A.13 in Appendix A shows faster segmental dynamics of HOS_t groups in the protected polymer, where hydrogen bonding and density are decreased (Figures 3.4 and 3.3), compared to the deprotected polymer in equilibrium simulations. As shown in Figure 6.2c, the model predicts that clustering is enhanced with H^+PFBS^- compared to H^+TFL^- . The increased clustering of H^+PFBS^- compared to H^+TFL^- is also consistent with the decreased hydrophilicity of PFBS^- ,^[106] suggesting that ion-ion interactions are induced by the increased hydrophobic fluorine content of PFBS^- . The ability to use this model to estimate clustering in CAR materials is important, as there is a significant impact of catalyst clustering on reaction rates observed in both experiments and simulations.

6.2.2 Model predictions of excess free volume generation

It is well established that diffusion of penetrants in polymers is enhanced by increased free volume.^[96, 97] In this section, we aim to connect the optimized diffusivities of the KMC model to the generation and relaxation of excess free volume. In prior literature,^[19] Croffie *et al.* proposed the use of a modified version of the Fujita-Doolittle equation to describe the elevation in catalyst diffusivities due to the hypothesized generation of excess free volume. This equation:

$$D = D_{\text{inert}} + D_0 \left(\exp \left(\frac{\omega \times \text{FEFV}}{1 + \nu \times \text{FEFV}} \right) - 1 \right) \quad (6.1)$$

where D is the elevated diffusivity, D_{inert} is the diffusivity in the absence of reaction, D_0 is the magnitude of elevation, FEFV is the fractional excess free volume, and ω and ν are empirical parameters; allows us to estimate fractional excess free volume from the model. By choosing the empirical parameters to be common literature values ($\omega = 10$, $\nu = 1$), and by setting the magnitude to be in the appropriate range for our observed diffusivities ($D_0 = 1 \times 10^{-17}$ cm²/s),^[19, 97] we obtain a relationship between local diffusivities and local FEFV. It is important to note, adjustments in the empirical parameter estimates for Equation 6.1 do

not alter the following qualitative results. Figure 6.3a provides a graphical representation of the Fujita-Doolittle equation using these assumed parameters. We then calculate the local FEFV for every lattice site from the local diffusivity as a function of time and sum all local FEFVs to obtain the global FEFV. Figure 6.3b provides the global FEFV calculated from the KMC model for 0.05, 0.08, and 0.11 $\#/\text{nm}^3$ H^+TFL^- at 340 K (Figure 6.1a). The optimized model predicts a maximum FEFV corresponding with a maximum in reaction rates, where the average diffusivity of all sites is also at a maximum. At long times the FEFV goes to zero as the reaction kinetics “plateau” and diffusivities become equivalent to the diffusivities in the equilibrium deprotected polymer. As the model uses the same parameters for all H^+TFL^- concentrations, the increased reaction rates at high catalyst concentrations creates more FEFV than lower concentrations.

Future work in this area will focus on connecting the FEFV predicted by the model to experimentally accessible metrics of the polymer system. The global thickness relaxation of the films during reaction is connected to FEFV, which could account for the slower rate of film thickness loss relative to reaction that was shown in Figure 4.2b. Therefore, the film was measured as a function of time for reacting films with 0.11, 0.08, and 0.05 $\#/\text{nm}^3$ H^+TFL^- using in-situ spectroscopic ellipsometry. The fractional thickness, z/z_0 , is the ratio of the instantaneous thickness, z , to the initial thickness, z_0 . Figure 6.3b also provides a comparison of the FEFV predicted by the model to z/z_0 of the reacting film samples at 340 K. In contrast to the FEFV calculated from the KMC model, z/z_0 does not display an initial increase. This is not unexpected as the model is not designed to display changes in density due to polymer composition or to model reaction byproducts that may be present at very early times prior to their escape from the film. z/z_0 also displays a linear dependence on $\log(\text{time})$ at the timescales where samples reach the “plateau” in deprotection level, which corresponds to a predicted FEFV of zero. Linear fits to this region are shown in Figure 6.3, and are thought to capture the glassy aging behavior of the polymer at its final composition.[107] At intermediate timescales, the decreases of predicted FEFV and measured z/z_0 follow the same trend. Interestingly, the final z/z_0 decreases with decreasing catalyst concentration, which is contrary to an expected increase in the final density at higher concentrations due to

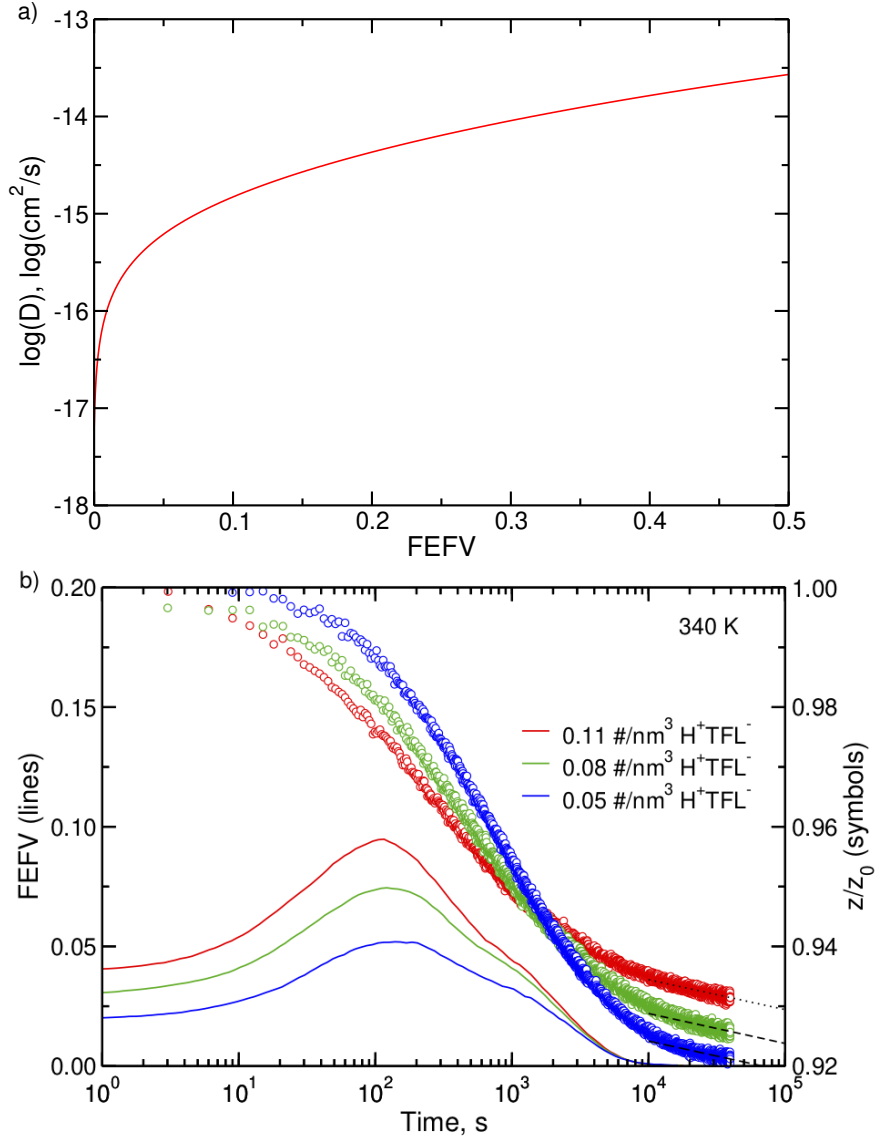


Figure 6.3: a) Relationship between diffusivity and FEFV as predicted by the Fujita-Doolittle equation using the proposed parameters. b) Global FEFV calculated from the predicted local diffusivities of the KMC model of reaction kinetics at 340 K with 0.05, 0.08, and 0.11 $\#/\text{nm}^3$ H^+TFL^- . z/z_0 obtained using spectroscopic ellipsometry as a function of time and H^+TFL^- concentration is also provided. Long-time linear dependence with $\log(\text{time})$ of z/z_0 represents glassy aging.

higher final deprotection levels. We hypothesize this may be the result of either: 1) higher resistances to film relaxation at high deprotection levels, as our prior simulations of the deprotected polymer show increased hydrogen bond interactions in the deprotected polymer than in the protected polymer; and 2) build-up of reaction byproducts that are trapped in the film during densification. To test this second point, TGA-MS was performed on reacting and inert films.

Figure 6.4 provides TGA-MS data for $0.11 \text{ \#}/\text{nm}^3 \text{ H}^+\text{TFL}^-$ in the initially protected polymer using the step-ramp-step temperature profile described in Section 6.1. The data show an approximate 3% loss in weight during the 1800 s anneal at 343 K. At these temperatures, the expected deprotection level at 1800 s is approximately 0.8. The temperature is then raised to 393 K where full deprotection is expected. During the ramp and hold at 393 K, mass spectrometry detects a significant release of 2-methylpropene and an approximate additional weight loss of 10%. The mass spectrometry data also indicates no release of PGMEA, which confirms removal of residual solvent during the pre-bake steps (prior to catalyst activation). As determined in Chapter 3, the T_g of the protected and deprotected polymers are 419 K and 436 K, respectively. Therefore, the presence of reaction byproducts in films could affect catalyst diffusion below the glass transition. These data indicate that 2-methylpropene is present in the film during reaction, which implies that volatilization of the byproducts is not immediate below T_g . 2-methylpropene is then able to escape once the film is heated to 393 K (closer to T_g). This is further supported by the smaller-than-expected weight loss during the isothermal anneal at 343 K, prior to the ramp to 393 K. While our KMC model of transient diffusivities does not directly incorporate reaction byproducts, any enhancement in local diffusivities of the catalyst due to reaction byproducts is captured by the model.

6.3 Conclusions

Our KMC model of accelerated diffusion was used to examine mechanisms that influence catalyst diffusion in CARS, which are not easily resolved through experiments. We examined

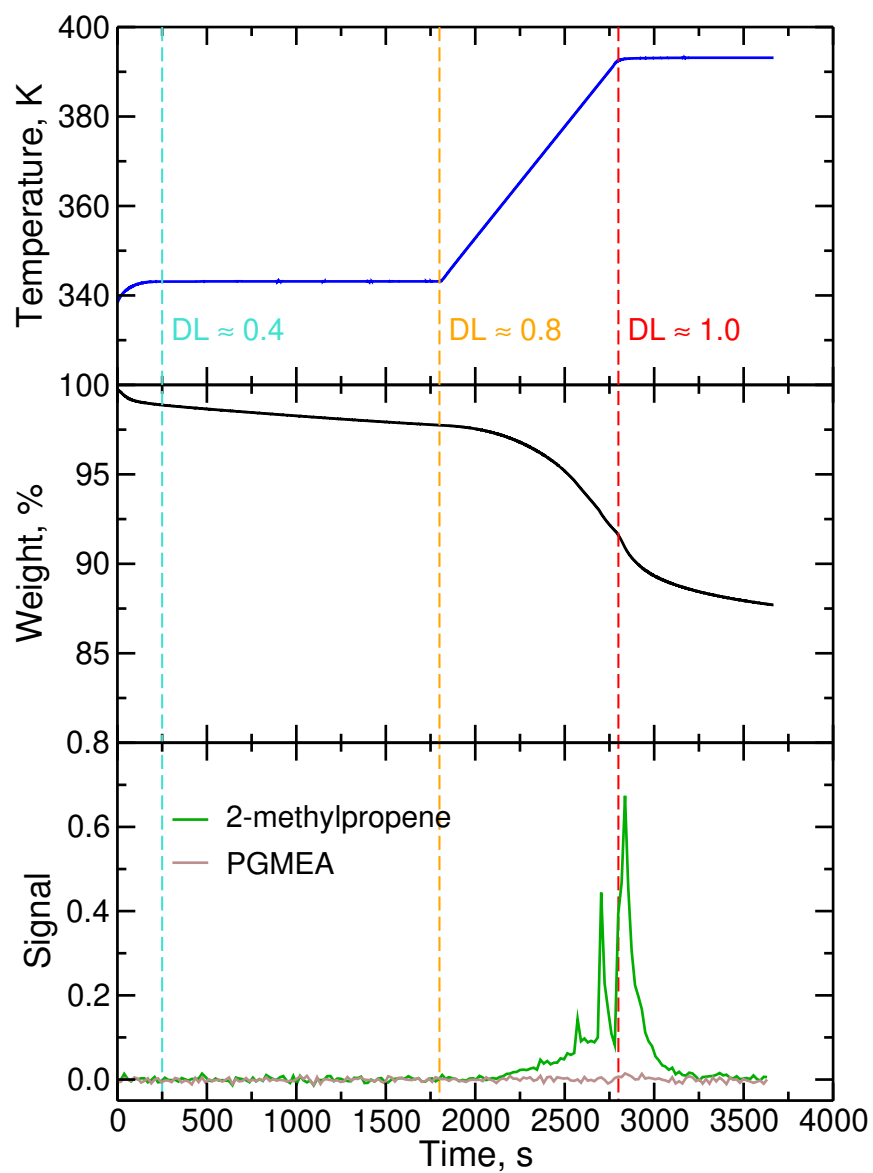


Figure 6.4: TGA-MS data of weight and signal intensity for a reaction byproduct (2-methylpropene) and the film casting solvent (PGMEA) for $0.11 \text{ \#}/\text{nm}^3 \text{ H}^+\text{TFL}^-$ in the initially protected polymer. Broken vertical lines indicate the approximate deprotection level at the 250, 1800, and 2800 s.

reaction kinetics in a terpolymer resin with two acid-anion catalysts to understand how counter-anion size contributes to local diffusivities, transition rates, and catalyst clustering. The model suggests that H^+PFBS^- has similar diffusivity in the terpolymer resin as H^+TFL^- , with a small increase in the transition rates. This suggests that transient local diffusion states relax towards equilibrium slightly faster in H^+PFBS^- , due a hypothesized increase in the segmental dynamics of the polymer. The model also predicts increased catalyst clustering in the H^+PFBS^- system which is justified by an expected increase in ion-ion interactions due to the increased fluorine content of PFBS^- anions compared to TFL^- . In addition, results of the model are used to estimate fractional excess free volume in the H^+TFL^- system using the Fujita-Doolittle equation. Fractional excess free volume reaches a maximum at similar timescales to the maximum in reaction and diffusion rates, and decays to zero at long times where diffusivities become equivalent to the diffusivities in the equilibrium deprotected polymer. Mass spectrometry measurements were performed of the volatilized reaction byproducts of the CAR system. These measurements support the presence of byproducts of reaction in the film during deprotection. These results suggests that both FEFV and reaction byproducts are contributing to accelerated catalyst diffusivities during reaction, albeit at difference timescales.

Chapter 7

Analysis of plasticization and reaction using TOF-SIMS

In prior studies, we performed direct measurements of the diffusion of an inert catalyst analogue,^[89] and determined that catalyst concentration and the composition of the polymer do not significantly impact catalyst diffusion in the absence of reaction. The prior chapters have shown that the reaction produces transient local diffusion states that accelerate catalyst diffusion before relaxing to the diffusivities in the absence of reaction. In addition, we have shown that byproducts of the reaction and excess free volume generated by their escape contribute to the formation of these accelerated local diffusivities. In this chapter, we employed TOF-SIMS to answer two final questions about catalyst diffusion in CARs: 1) Does plasticization of the polymer by photoactivation byproducts contribute to catalyst diffusion?; and 2) What are the impacts of temperature and catalyst concentration on the spatial extent of diffusion and reaction in bilayers?

7.1 Methods

Preparation of Bilayer Samples. Bilayer samples consisted of a base “feeder layer” and a top “diffusion layer” on silicon and were prepared as described in Chapter 3. The feeder

layer was a blend of polymer and either Na^+TFL^- or H^+TFL^- (loading of 0.05 or 0.11 $\#/\text{nm}^3$), and the diffusion layer was the same polymer without ionic penetrant. The polymer was either the protected or deprotected polymer. The diffusion layer was transferred on top of the feeder layer by stamping with a PDMS stamp. Samples of the deprotected polymer with Na^+TFL^- with the addition of a common industrial plasticizer, dioctyl phthalate (DOP), were also prepared. Feeder layers for these samples consisted of the deprotected polymer containing 0.11 $\#/\text{nm}^3$ Na^+TFL^- and 0.11 $\#/\text{nm}^3$ DOP (referred to as $\text{Na}^+\text{TFL}^- + \text{DOP}$) to serve as a model of plasticization of the polymer due to photoactivation byproducts. Diffusion layers for $\text{Na}^+\text{TFL}^- + \text{DOP}$ samples consisted of the deprotected polymer. The thicknesses of the base layer and the bilayer were measured with a J.A. Woollam M-2000 spectroscopic ellipsometer and analyzed using CompleteEASE software as described in Chapter 3.

Depth-Dependent Composition of Catalysts in Bilayers. The depth profiles of Na^+TFL^- and H^+TFL^- were analyzed using the TOF-SIMS NCS system described in Chapter 3. TOF-SIMS data were collected in the form of ion signal versus sputter time. For bilayers consisting of polymer with Na^+TFL^- or $\text{Na}^+\text{TFL}^- + \text{DOP}$, the prior depth and concentration calibration protocols were used, as described in Chapter 3. For bilayers containing H^+TFL^- , the same depth calibration protocol was performed however a new concentration calibration was prepared. As shown in Figure 7.1a, the four ion signals of interest were 1) Si^- , unique to the substrate; 2) F^- , unique to the catalyst and substrate; 3) C_4H_9^- , unique to tBA repeat units; and 4) O^- . The O^- signal is not a unique signal. However in TOF-SIMS, elemental signals are often not sensitive to composition, which allows for the determination of catalyst concentration independent of polymer composition. Calibration samples of single layer films of H^+TFL^- in the initially protected polymer were prepared in a range of catalyst concentrations and baked to obtain a range of deprotection levels, determined through FTIR. Calibration samples of the fully deprotected polymer, obtained through chemical deprotection, with H^+TFL^- were also prepared. As shown in Figure 7.1b, the ratio of F^- to O^- in these calibration samples is linearly dependent on the number density of H^+TFL^- and independent of polymer composition (deprotection level). Figure 7.1c shows

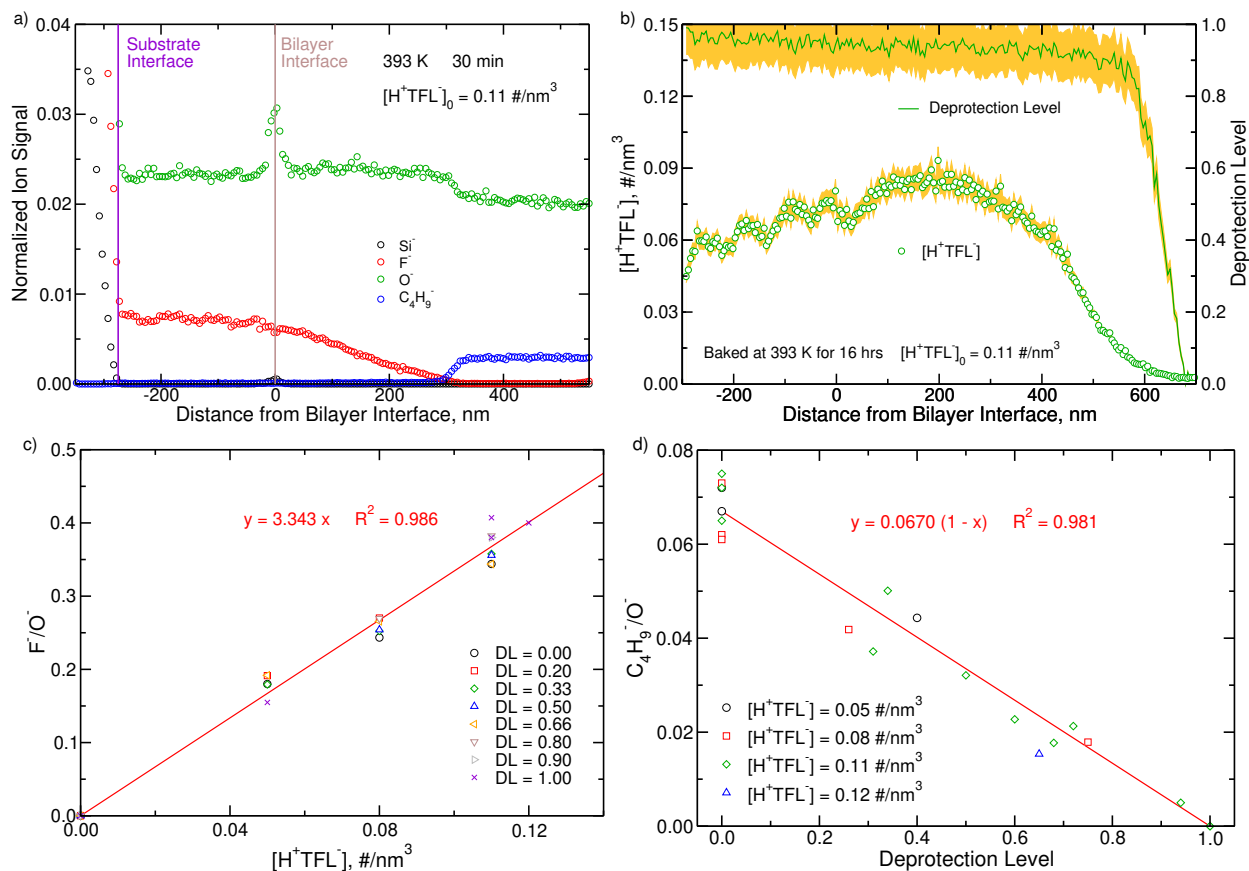


Figure 7.1: a) Normalized ion signals as a function of distance from the bilayer interface for a reacting bilayer sample annealed at 393 K for 30 min with an initial feeder layer concentration of $0.11 \text{ \#/nm}^3$ H^+TFL^- . Vertical lines denote the substrate and bilayer interfaces. b) Representative TOF-SIMS data of depth dependent H^+TFL^- concentration (calculated from calibration curve in c) and deprotection level (calculated from calibration curve in d) for the same reacting bilayer sample. Gold shaded regions provide the 95% confidence interval on data points. c) F^-/O^- as a function of H^+TFL^- concentration. Calibration curve and equation are provided. DL indicates the deprotection level of the calibration samples. d) $\text{C}_4\text{H}_9^-/\text{O}^-$ as a function of deprotection level for annealed calibration samples at a variety of catalyst concentrations. Calibration curve and equation are provided.

the linear relationship between the ratio of C_4H_9^- to O^- and deprotection level in these calibration samples. These calibration curves allow for the analysis of the spatial distribution of the catalyst concurrent with the analysis of deprotection fronts, as shown in Figure 7.1d.

7.2 Results

7.2.1 Catalyst activation byproducts

The aim of this section is to determine if catalyst activation byproducts impact catalyst diffusion. In polymers, plasticizers are molecules that lower the glass transition and decrease the density of the polymer at temperatures below T_g . Plasticization of the polymer in a polymer-penetrant system is also known to increase penetrant diffusion.[108, 109] The decomposition of the photoacid generator upon exposure to UV light generates a variety of photoactivation byproducts, as shown in Figure 2.1. Many of these byproducts are expected to be non-volatile due to their low vapor pressures and contain bulky phenyl groups with similar chemical structure to many common plasticizers. Therefore, diffusion of the catalyst may be impacted by plasticization of the resist due to the production of photoactivation byproducts.

To examine whether photoactivation byproducts might act as plasticizers, we add Na^+TFL^- and equal amounts of a common industrial plasticizer, DOP, to the feeder layers of bilayers consisting of the deprotected polymer. Diffusion fronts of Na^+TFL^- in this plasticized system are compared to diffusion fronts of Na^+TFL^- in the deprotected polymer, and to diffusion fronts of H^+TFL^- in the deprotected polymer. H^+TFL^- is generated from the TPS-TFL PAG, which produces photoactivation byproducts in the feeder layer. Figure 7.2 shows a comparison of penetrant diffusion in samples annealed at 393 K for 16 hr of the deprotected polymer with $0.11 \text{ \#}/\text{nm}^3$ of $\text{Na}^+\text{TFL}^- + \text{DOP}$, of Na^+TFL^- , and of H^+TFL^- . At 393 K, the diffusion length (L_D) of H^+TFL^- is 120 nm which is roughly twice the L_D (60nm) of Na^+TFL^- . With the addition of DOP, the diffusion front of Na^+TFL^- is enhanced ($L_D = 140 \text{ nm}$) when compared to Na^+TFL^- without DOP and closely mimics the L_D of

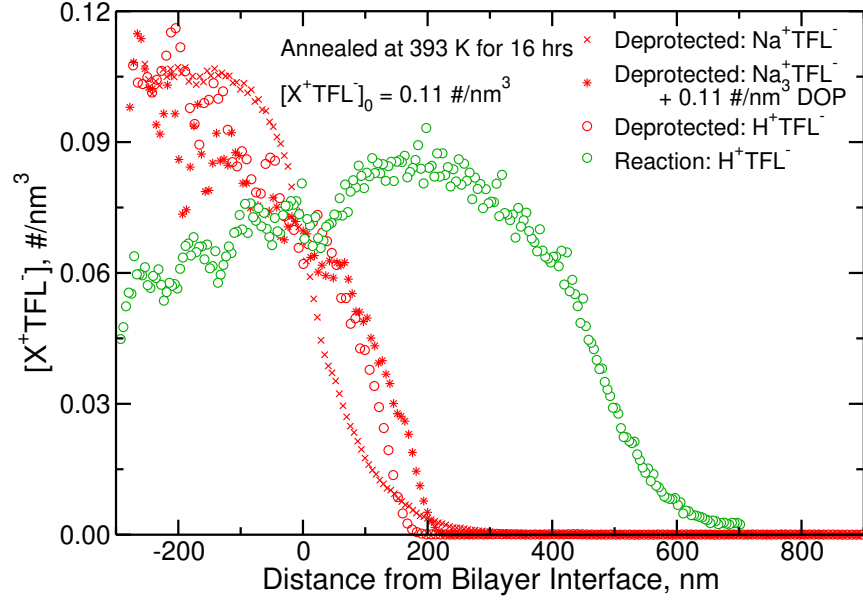


Figure 7.2: Representative TOF-SIMS data of depth dependent X^+TFL^- concentration (where X^+ indicates either Na^+ or H^+) for annealed bilayer samples (393 K for 16 hr) of the deprotected polymer with $0.11 \text{ \#}/\text{nm}^3$ Na^+TFL^- , of the initially protected polymer (terpolymer resist) with $0.11 \text{ \#}/\text{nm}^3$ H^+TFL^- generated from TPS-TFL (indicated as Reaction), of the deprotected polymer with $0.11 \text{ \#}/\text{nm}^3$ H^+TFL^- , and of the deprotected polymer with $0.11 \text{ \#}/\text{nm}^3$ Na^+TFL^- and $0.11 \text{ \#}/\text{nm}^3$ DOP.

H^+TFL^- , as well as the deviations of the diffusion front from Fickian diffusion.[83] This result suggests that the byproducts produced during photoactivation are plasticizing the polymer in a similar manner to the industrial plasticizer, which promotes catalyst diffusion.

7.2.2 TOF-SIMS of reacting bilayers

We established that photoactivation byproducts enhanced catalyst diffusion, however it is important to know how this enhancement compares with catalyst diffusion during reaction. Bilayer samples were created with a feeder layer that consisted of TPS-TFL and the protected polymer (referred to as the terpolymer resist). Diffusion layers for these bilayers consisted of solely the protected polymer. H^+TFL^- was generated in film by exposing the bilayers to UV light. Upon annealing, the catalyst diffuses and promotes deprotection. TOF-SIMS was used to analyze the depth-dependent distribution of the catalyst in bilayer films post annealing.

As shown in Figure 7.1d, the L_D of the active catalyst is approximately 500 nm in the terpolymer resist and approximately 120 nm in the deprotected polymer after 16 hours at 393 K. This indicates a significant enhancement in catalyst diffusion in the reacting bilayer, which indicates that plasticization due to photoactivation byproducts only play a minor role in enhanced catalyst diffusion. This also confirms that catalyst diffusivities are significantly accelerated during reaction, consistent with the atomistic simulations with material relaxation and the KMC model of transient diffusivities. Diffusion fronts in the absence of reaction were well described by Fick’s second law. However, diffusion fronts in reacting bilayers deviate from Fickian diffusion. This supports the presence of transient spatially-dependent diffusivities.

To further understand the interplay between reaction and catalyst diffusion, bilayer samples of the terpolymer resist were created with 0.05 and 0.11 $\#/\text{nm}^3$ H^+TFL^- in the feeder layer. These samples were annealed at temperatures in the range of 393 - 363 K for 10 - 960 min. Figure 7.3a shows a time series of reacting bilayers annealed at 393 K with 0.11 $\#/\text{nm}^3$ H^+TFL^- . The depth-dependent catalyst concentration was calculated using

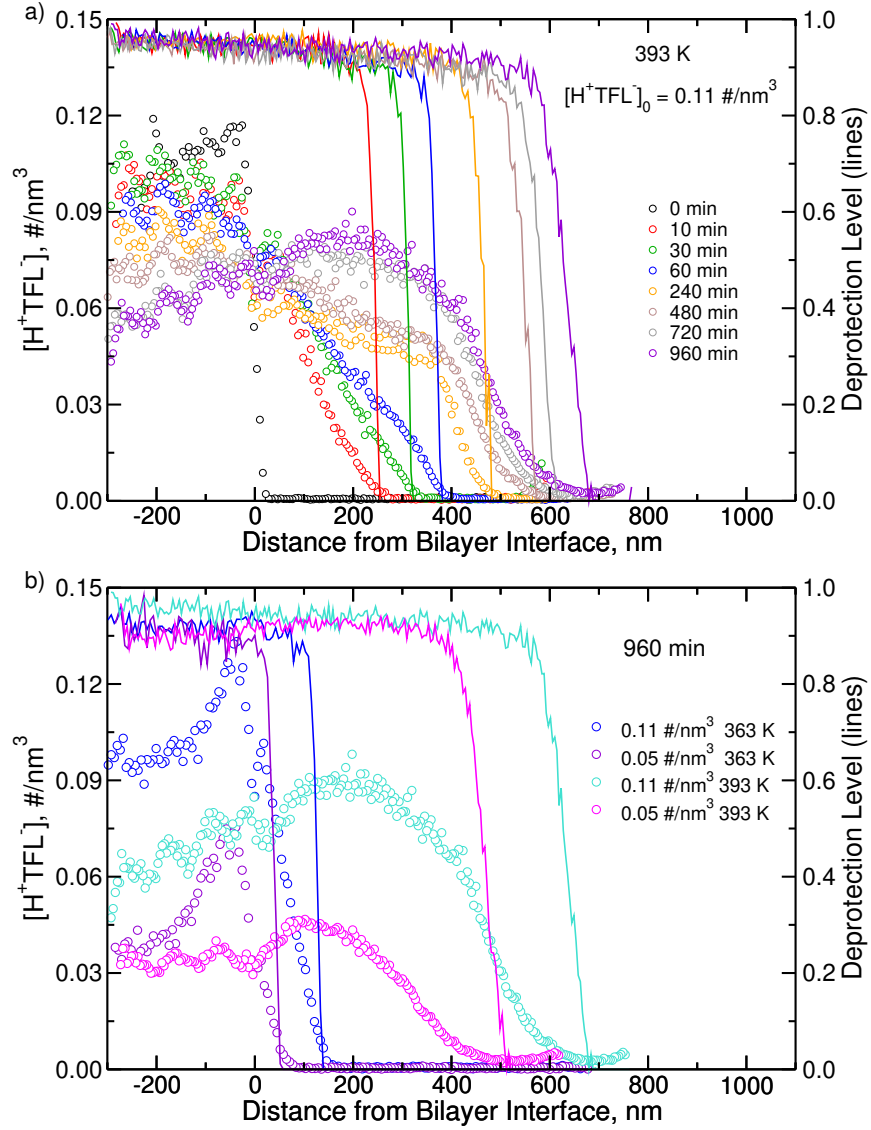


Figure 7.3: a) Concentration of H^+TFL^- (symbols) and deprotection level (lines) as a function of distance from the bilayer interface for samples annealed at 393 K over a range of times. b) The same for samples annealed for 960 min at 373 K and 393 K with initial feeder layer concentrations of 0.05 and 0.11 $\text{\#}/\text{nm}^3$ H^+TFL^- .

the calibration curve in Figure 7.1c, and the depth-dependent deprotection level in these samples was calculated using the calibration curve in Figure 7.1d. Figure 7.3b shows depth profiles of catalyst concentration and deprotection levels at two temperatures but the same annealing time (363 K and 393 K annealed for 980 min), along with the corresponding deprotection level profiles. In all reacting bilayer samples, the catalyst diffusion front appears to lag the deprotection front. This demonstrates that reaction enhances diffusion at the deprotection front, which promotes further propagation of the diffusion front. While Na^+TFL^- concentration did not have an impact on diffusion in the absence of reaction, in reacting bilayers, reduced concentration of H^+TFL^- in the feeder layer slowed the propagation of the deprotection front and the diffusion front. We note that, reacting bilayer samples at 363 K display a small buildup of H^+TFL^- near the bilayer interface that is not present in control samples prior to annealing. This may indicate some resistance to diffusion at the bilayer interface at low temperatures, however further study is necessary to determine the origin of this build-up.

Estimates of the L_D , the deprotection length (L_{dep}), and the width of the deprotection front (γ) in annealed reacting bilayer samples were used to compare samples as a function of annealing time, temperature, and catalyst concentration. As diffusion fronts vary in shape across annealing times, the L_D were estimated to be the distance from the bilayer interface at a catalyst concentration that is 33% of the initial catalyst concentration (0.036 and 0.017 $\#/\text{nm}^3$ for 0.11 and 0.05 $\#/\text{nm}^3$, respectively). To analyze the characteristics of the deprotection front, the derivative was calculated for each deprotection profile and fit with a Gaussian distribution. The L_{dep} and γ were taken as the center and full width at half maximum of the Gaussian distribution, respectively. The experimental resolution limit of TOF-SIMS in our bilayer samples was determined to be approximately 20 nm (Section A.8), this resolution limit contributes to the estimated values of γ and γ smaller than 20 nm cannot be resolved. Figure 7.4a provides L_{dep} , L_D , and γ for the time series of reacting bilayers annealed at 393 K with 0.11 $\#/\text{nm}^3$ H^+TFL^- . Figure 7.4b provides L_{dep} , L_D , and γ for the samples of both catalyst concentrations at 363 K and 393 K annealed for 980 min. L_{dep} and L_D are observed to increase with increasing annealing time and temperature. Fick's second

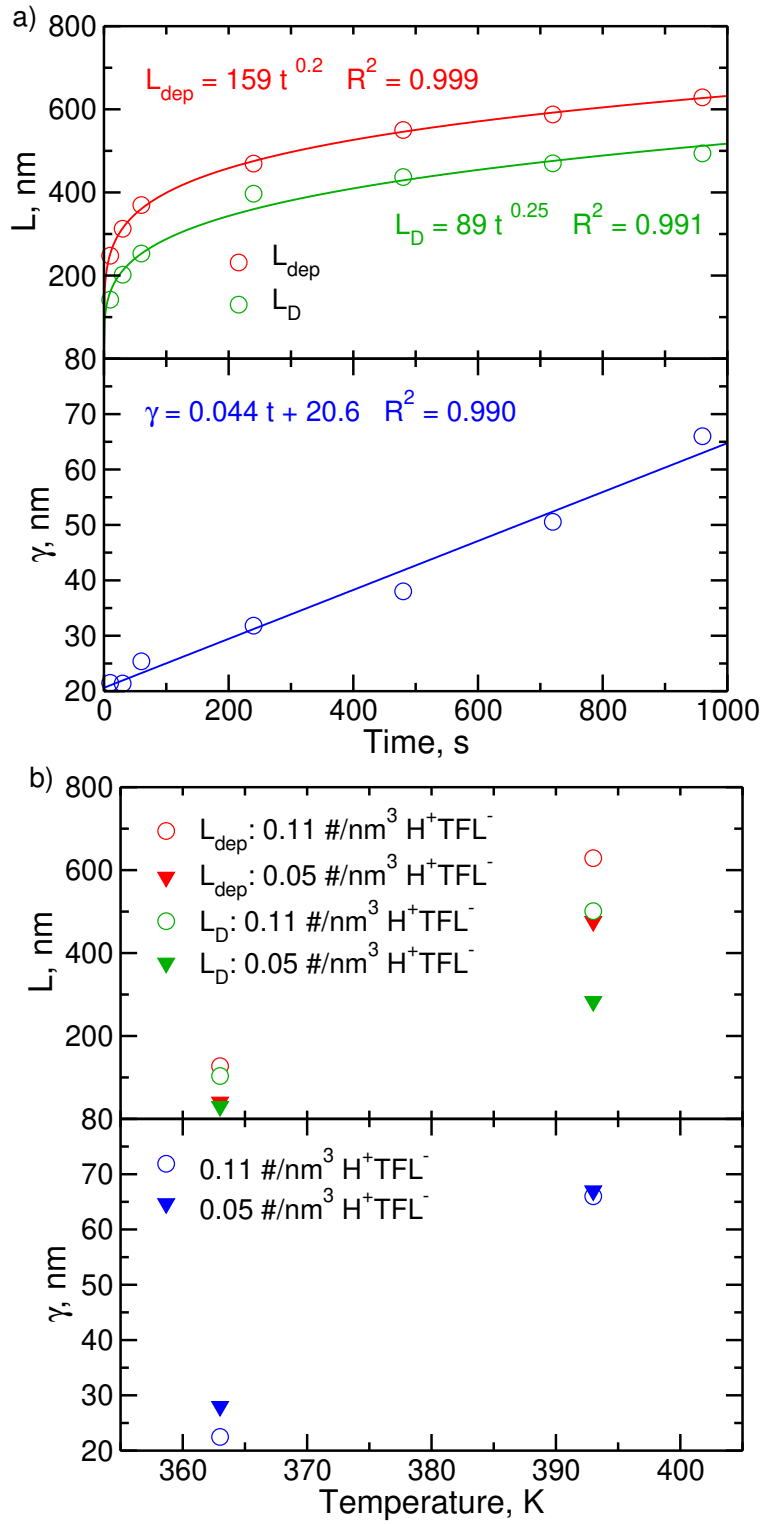


Figure 7.4: a) L_D , L_{dep} , and γ as a function of annealing time at 393 K of the reacting bilayer samples, shown in Figure 7.3a. Best-fit power scaling (lines) and equations are provided for L_{dep} and L_D . A linear best-fit model (line) and equation are provided for γ . b) L_D , L_{dep} , and γ as a function of temperature with an initial feeder layer concentration of 0.05 (closed symbols) and 0.11 (open symbols) H⁺TFL⁻, these data correspond to Figure 7.3b.

law predicts that L_D should scale linearly with $t^{0.5}$, but a $t^{0.25}$ scaling is observed, which indicates that diffusivities are slowing as the diffusion fronts move farther from the bilayer interface. In addition, γ is observed to increase with increasing L_D and decreasing catalyst concentration. It is likely that these two effects are coupled: As the L_D increases, the catalyst concentration close to the deprotection front continues to decrease, which lowers reaction rates and slows diffusion rates at the deprotection front over time. This could also contribute to the increase in γ at increased L_D , as these transient global diffusivities are likely linked to the expected heterogeneous distribution of protecting groups and local diffusivities at the molecular length scale. Heterogeneous Na^+TFL^- dynamics were observed in both simulations with material relaxation and equilibrium simulations (Figure 3.6a), which suggests an increased disparity in the single catalyst displacements as the catalysts explore more of the material with increasing time.

7.2.3 Bilayer KMC of reaction and diffusion

Ongoing work has begun on the characterization of spatial reaction and diffusion using the KMC model of accelerated diffusivities. The geometry of the KMC model was altered to model bilayer samples using a lattice framework of $20 \times 20 \times 650$ ($x \times y \times z$) cubic lattice sites of 1 nm^3 volume. Reflective boundary conditions were applied in the z dimension and catalyst probes were initially inserted in the first 280 lattice sites in the z dimension. In this case, the bilayer interface occurs between the 280 and 281 position in the z dimension. Parameters for the model (D_2 , D_1 , k_2 , k_1 , α) were the same as the best-fit parameters for bulk reaction kinetics models of H^+TFL^- at 350 K (Figure 5.3). Figure 7.5 provides the model predictions of H^+TFL^- concentration and deprotection level as a function of distance from the bilayer interface for using these parameters for a range of times (12 - 6000 hr). The catalyst concentration of $0.082 \text{ \#}/\text{nm}^3$ H^+TFL^- corresponds to the optimized α (cluster size) of 1.373. L_D and L_{dep} progress in a manner that is similar to experimental reacting bilayer samples, however the model predicts a γ of 60 nm at a L_{dep} of 60 nm, where deprotection fronts are expected to be sharp. This is a result of the implemented instantaneous reaction in

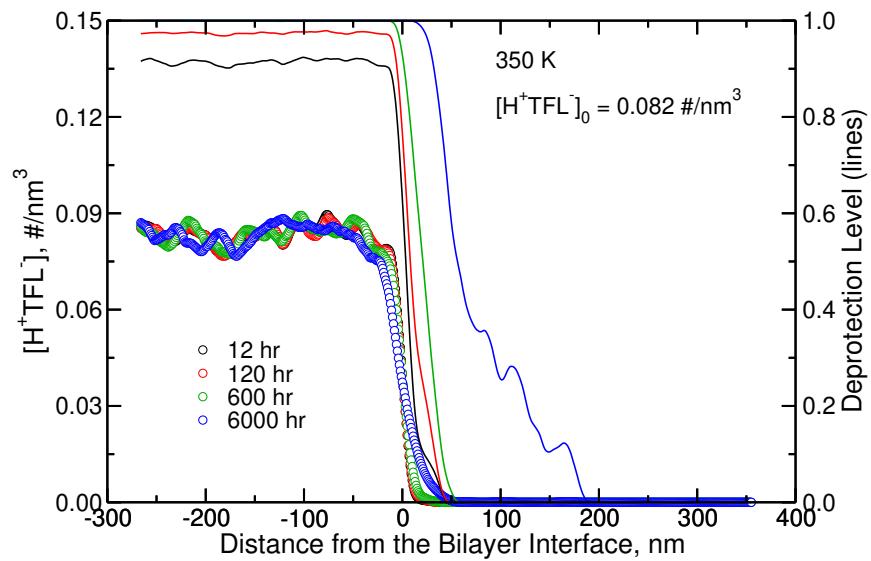


Figure 7.5: H^+TFL^- concentration (symbols) and deprotection level (lines) for a bilayer model of reaction at 350 K with 0.082 $\#/\text{nm}^3$ H^+TFL^- as a function of anneal time. This model corresponds to the optimized KMC parameters (including clustering) for reaction kinetics with 0.11 $\#/\text{nm}^3$ H^+TFL^- at 350 K (Figure 5.3).

the model promoting a small amount of catalyst probes to propagate significantly farther than most probes. Another fitting parameter of a fast, but finite, reaction rate will likely need to be incorporated in the model to limit this effect, so that bilayer models can be optimized to predict the catalyst diffusion and reaction in TOF-SIMS measurements. We note that, the model predicts an annealing time of >600 hr would be necessary observe significant reaction and catalyst diffusion at 350 K. Therefore, the Arrhenius temperature dependence of the KMC parameters observed in Figure 5.3 will be used to estimate initial parameters at higher temperatures, that will be optimized to match the predictions of the bilayer KMC model to the shape of the diffusion front, L_D , L_{dep} , and γ observed in the reacting bilayers (Figures 7.3 and 7.4).

7.3 Conclusions

TOF-SIMS was used to determine if photoactivation byproducts plasticize the polymer and contribute to enhanced catalyst diffusion. Bilayers of the deprotected polymer containing Na^+TFL^- and a common industrial plasticizer were found to mimic diffusion fronts in bilayers of the deprotected polymer containing H^+TFL^- (without reaction) and photoactivation byproducts. This indicated that photoactivation byproducts produced during catalyst activation are acting as plasticizers in our CAR system. Diffusion fronts in bilayers of the terpolymer resist containing H^+TFL^- (with reaction) and photoactivation byproducts were significantly enhanced relative to diffusion fronts in the absence of reaction. This demonstrated that, while plasticization of the polymer due to photoactivation byproducts plays a minor role, transient states produced by the reaction significantly elevate catalyst diffusivities. TOF-SIMS was also used to analyze the effects of temperature and catalyst concentration on catalyst diffusion and deprotection fronts in bilayers of the terpolymer resist. Diffusion lengths and deprotection front propagation both increased with increasing time, increasing catalyst concentration, and increasing temperature. The width of the deprotection front increased with increasing diffusion lengths and decreasing catalyst concentration. These effects are suspected to be the result of heterogeneous catalyst diffusion

lengths produced by the local distribution of protecting groups within the film. The KMC model of transient diffusivities was extended to a bilayer system and displays similar scaling of diffusion fronts and deprotection fronts with time. However, further modification is necessary to model the spatial dependence of catalyst diffusion and reaction in these bilayer systems, as the model overestimates the width of the deprotection front.

Chapter 8

Conclusions and Outlook

This dissertation presents a combined experimental and simulation approach to studying the physical processes that control catalyst diffusion during reaction in a model CAR based on P(HOSt-tBA-St). In CARs, the complex interplay between the reacting polymer matrix and the diffusion of the catalyst is not well understood, which makes it difficult to predict and control catalyst diffusion and the spatial extent of deprotection. While it is well established that reaction is controlled by catalyst diffusion, it is difficult to quantify catalyst diffusivities through direct measurements, especially at nanometer length scales. It is even more challenging to examine the role of polymer-ion and ion-ion interactions and the role of polymer densification on catalyst mobility. Herein, we addressed these challenges through systematic studies with a model CAR that allowed us to interrogate the controlling factors of catalyst diffusion in the presence and absence of reaction.

Prior literature studies used a composition-dependent diffusivity to describe reaction kinetics, but offered little justification for the use of such a model. We developed an inert CAR system to examine the effects of polymer composition on catalyst diffusion, and found that catalyst diffusion in the absence of reaction is independent of polymer composition and catalyst concentration below T_g . The catalyst diffusivities in this inert system were found to be orders-of-magnitude slower than the catalyst diffusivities predicted by models of reaction kinetics. This is consistent with prior literature that indirectly measured catalyst diffusion in

inert analogues of the polymer. These studies suggested that reaction promotes the diffusion of the catalyst. To determine if the accelerated catalyst diffusivities could be directly produced by the reaction, atomistic simulations were performed to observe the material relaxation that occurs after removal of protecting groups. These simulations demonstrate that catalyst diffusion is accelerated by the local transient states produced by the reaction, and that excess free volume generated by the reaction can significantly accelerate both catalyst and polymer dynamics. In addition, catalyst clustering was shown to significantly impact reaction rates, which in turn influences catalyst diffusivities during reaction.

A kinetic Monte Carlo model of transient local catalyst diffusivities was developed, and captures reaction kinetics observed in simulations ($T \gg T_g$) and experiments ($T < T_g$). The model supports that catalyst clustering can capture deviations from the expected catalyst concentration scaling observed in reaction kinetics. The model was applied to study the effect of increased counter-anion size on reaction kinetics and to provide estimates of excess free volume generation below T_g . Increased counter-anion size was found to increase catalyst clustering, but had little effect on the accelerated local diffusivities and transition rates. Estimates of the excess free volume predicted by the model and measurements of volatilized byproducts during reaction, suggest that both reaction byproducts and the excess free volume contribute to accelerated catalyst diffusivities below T_g , albeit at different timescales.

To determine if plasticization of the polymer by photoactivation byproducts could also play a role in accelerated catalyst diffusion, bilayer samples of the deprotected polymer (in the absence of reaction) were created with the active catalyst (with photoactivation byproducts) and with the inert catalyst analogue with the addition of a common industrial plasticizer. Diffusion fronts of inert catalyst analogue with the plasticizer mimicked diffusion fronts of the active catalyst, demonstrating that photoactivation byproducts plasticize the polymer and promote catalyst diffusion. However, measurements of the diffusion front of the active catalyst in the terpolymer resist (with reaction) demonstrate diffusion lengths that were over four times higher than diffusion lengths in inert samples, further indicating that excess free volume and reaction byproducts produce the significant accelerated diffusivities during reaction.

Concurrent measurements of diffusion and reaction fronts were used to analyze the effects of temperature and catalyst concentration on the reaction and diffusion in bilayers. The propagation of diffusion fronts and reaction fronts over time suggest that diffusivities slow and the width of the deprotection front increases as the diffusion front moves farther from the bilayer interface. This suggests the contribution of heterogeneous catalyst diffusion lengths, which is supported by the heterogeneous dynamics of catalysts observed in the atomistic simulations. Modeling efforts to connect the diffusion fronts and reaction fronts to accelerated local diffusivities and catalyst clustering are ongoing.

This experimental and computational approach has made significant progress in interrogating the underlying physical and chemical processes that control catalyst diffusion in this model CAR system. P(HOSt-tBA-St) and the two catalysts studied herein are industrially relevant CAR chemistries, however many of the highlighted results are system specific, as changing the chemistry of the resin or catalyst could impact these observations. Importantly, the employed methodologies are transferable to other CAR chemistries, and can be used for the development of predictive models of reaction kinetics and catalyst diffusion in these other systems. Such models would support the development of new CAR materials by providing a means of gathering molecular-level data that is often inaccessible through experimental methods.

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Appendix A

Appendix

A.1 Gel permeation chromatography (GPC)

The molecular weight and dispersity of P(HOSt-tBA-St) were assessed using a Tosoh EcoSEC with a three column system of two Tosoh TSKgel SuperMultipore HZ-M (4.6×150 mm, $4 \mu\text{m}$) columns and a TSKgel SuperMultipore HZ-M guard. Data was collected with both the RI and UV detectors at 313 K. THF was used as the mobile phase with a flow rate of 0.35 mL/min at 313 K. Molecular weights were calculated relative to PS standards with a calibration range from 600 to 7,500,000 g/mol. The GPC trace data are summarized in Figure A.1. For the RI detector, a weight-average molecular weight of 7.0 kg/mol with a dispersity of 1.6 was determined. For the UV detector, a weight-average molecular weight of 6.6 kg/mol with a dispersity of 1.7 was determined.

A.2 Hydrogen nuclear magnetic resonance (^1H -NMR) spectroscopy

^1H -NMR spectras of P(HOSt-tBA-St) and chemically deprotected P(HOSt-AA-St) were obtained using a Varian VNMRS 500MHz spectrometer with a solvent of dimethyl sulfoxide- d_6 (DMSO- d_6). P(HOSt-tBA-St) composition, determined from the data in Figure A.2a, was

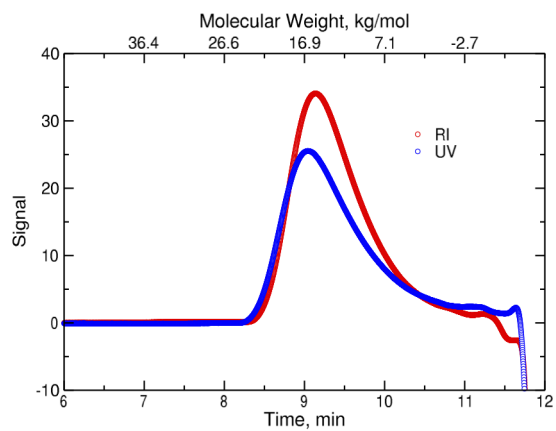


Figure A.1: GPC trace of P(HOSt-tBA-St).

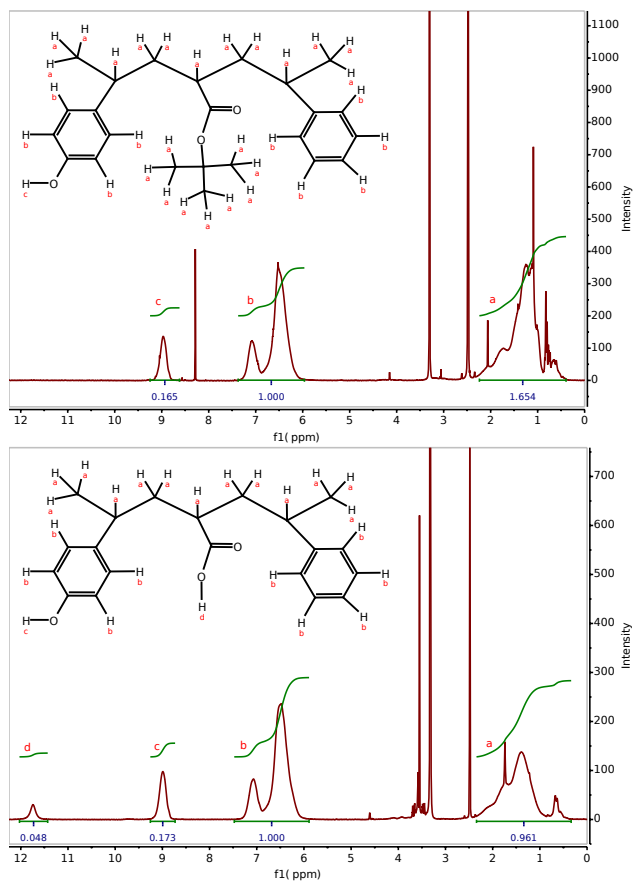


Figure A.2: ^1H -NMR Data of P(HOSt-tBA-St) (top) and P(HOSt-AA-St) (bottom)

found to be 55%-25%-20% by mole. Conversion of tBA to AA, determined from the data in Figure A.2b, was determined to be 99% by tracking the loss of the strong peak at 1.09 ppm which originates from the tert-butyl group in tBA. Trace contaminants of dimethyl sulfoxide (2.50 ppm) and water (3.33 ppm), both present from DMSO-d₆ absorbing and proton exchanging with water from the air, are present in each ¹H-NMR spectra and trace contaminant of 1,4-dioxane (3.57 ppm) in P(HOSt-AA-St) is detectable, but weak.

A.3 Molecular dynamics forcefield parameters

The parameters for Lennard-Jones and Coulombic interactions as well as the intramolecular terms of the forcefield associated with bonds, angles, and dihedrals parameters are summarized in Tables A.1, A.2, A.3, and A.4.

A.4 Chain dynamics and monomeric friction

The polymer dynamics in the 0.11 #/nm³ Na⁺TFL⁻ P(HOSt-AA-St) system at 470, 520, and 570 K were analyzed through the mean-square displacement of polymer atoms and the center of mass of chains. Figure A.3 shows that the trajectories at 570 and 520 K are sufficiently long to observe a convergence in the difference between the average displacements of individual polymer atoms and the displacements of the center of masses of polymer chains. At 470 K this has not occurred within the 10 μ s simulations performed. Using the equation:

$$\zeta_D = \frac{k_B T}{ND} \tag{A.1}$$

where k_B is the Boltzmann constant, T is temperature, N is the number of polymer repeat units, and D is the diffusivity; the monomeric friction coefficient ζ_D was calculated as displayed in Figures A.3a-c. The values extracted are also compared to experiment data of 12 kg/mol polystyrene at all temperatures using the difference from the experimental glass

Table A.1: Forcefield parameters for non-bonded interactions of polymers and penetrant in atomistic simulations.

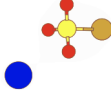
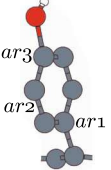
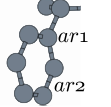
Non-bonded Interactions				
Name and Structure	Atom/Group	q_i (e)	σ_{ii} (Å)	ϵ_{ii}/k_b (K)
Na-TFL 	CF ₃	-0.138	4.472	80.5
	S	0.694	3.564	125.8
	O	-0.452	2.960	105.7
	Na	0.800	3.300	1.4
HOSt 	CH ₂	0.000	3.950	46.0
	CH	0.000	4.650	10.0
	CH _{ar1}	0.000	3.700	30.0
	CH _{ar2}	0.000	3.695	50.5
	CH _{ar3}	0.265	4.333	10.0
	O	-0.700	3.020	93.0
	H	0.435	0.000	0.0
St 	CH ₂	0.000	3.95	46.0
	CH	0.000	4.65	10.0
	CH _{ar1}	0.000	3.700	30.0
	CH _{ar2}	0.000	3.695	50.5
tBA 	CH ₂	0.000	3.95	46.0
	CH	0.000	4.65	10.0
	C=(O)	0.400	3.820	40.0
	O=(C)	-0.400	3.050	79.0
	O	-0.250	2.800	55.0
	C	0.250	5.800	0.5
AA 	CH ₂	0.000	3.95	46.0
	CH	0.120	4.65	10.0
	C=(O)	0.420	3.900	41.0
	O=(C)	-0.450	3.050	79.0
	O	-0.460	3.020	93.0
	H	0.370	0.000	0.0
Chain Ends	CH ₃	0.000	3.750	98.0

Table A.2: United-Atom forcefield parameters for bond lengths of polymers and penetrant in atomistic simulations.

Bond Lengths		
Name	Bond	Length (Å)
TFL	CF ₃ –S	2.400
	O–S	1.450
HOS _t	CH ₂ –CH	1.540
	CH ₂ –C _{ar}	1.510
	CH _{ar} –CH _{ar}	1.400
	C–O	1.360
	O–H	0.945
St	CH ₂ –CH	1.540
	CH ₂ –C _{ar}	1.510
	CH _{ar} –CH _{ar}	1.400
tBA	CH ₂ –CH	1.540
	CH ₂ –COO	1.520
	CO=O	1.200
	CO–O	1.344
	O–C	1.410
	C–CH ₃	1.540
AA	CH ₂ –CH	1.540
	CH ₂ –COO	1.520
	CO=O	1.200
	CO–O	1.344
	O–H	0.970

Table A.3: United-Atom forcefield parameters for bond angles and bending constants of polymers and penetrant in atomistic simulations, where θ is the angle between atoms ijk .

Bond Angles and Bending Constants $V_a(\theta_{ijk}) = \frac{1}{2}k_\theta(\theta - \theta_0)^2$			
Name	Bend	θ_0 ($^\circ$)	k_θ (kJmol $^{-1}$ rad $^{-2}$)
TFL	O-S-CF $_3$	103.2	640.152
	O-S-O	114.6	624.253
HOSt	CH $_i$ -CH-CH $_j$	109.5	520.000
	CH $_i$ -C $_{ar}$ -CH $_{ar}$	109.5	520.000
	C $_{ar}$ -CH $_{ar}$ -CH $_{ar}$	120.0	1000.00
	CH $_{ar}$ -C $_{ar}$ -O	122.5	335.000
	C $_{ar}$ -O-H	113.0	146.000
St	CH $_i$ -CH-CH $_j$	109.5	520.000
	CH $_i$ -C $_{ar}$ -CH $_{ar}$	109.5	520.000
	C $_{ar}$ -CH $_{ar}$ -CH $_{ar}$	120.0	1000.00
tBA	CH $_i$ -CH-CH $_j$	109.5	520.000
	CH $_2$ -CH-COO	109.5	520.000
	CH-C=O	126.0	335.000
	CH-C-O	111.0	293.500
	CO-O-C	115.0	520.000
	O-C-CH $_3$	111.0	294.000
AA	CH $_i$ -CH-CH $_j$	109.5	520.000
	CH $_2$ -CH-COO	109.5	520.000
	CH-C=O	126.0	335.000
	CH-C-O	111.0	293.500
	CO-O-H	107.0	146.000

Table A.4: Forcefield parameters and equations for dihedrals of polymers in atomistic simulations, where ϕ and ξ are the angle between ijk and jkl planes of bonded atom sequence $ijkl$.

Improper Dihedrals $V_{id}(\xi_{ijkl}) = \frac{1}{2}k_{\xi}(\xi - \xi_0)^2$			
Name	Dihedral	ξ_0 (°)	k_{ξ} (kJ/mol*rad ²)
Pendant	CH-CH ₂ -CH-C	35.26	334.8
HOS _t /St	CH _{ar} -C _{ar} -CH _{ar} -CH _{ar}	0.0	167.4
AA	CH-CH ₂ -CH-O	0.0	167.4
AA	CH ₂ -CH-O-H	0.0	167.4

Proper Dihedrals $V_d(\phi_{ijkl}) = k_{\phi}(1 + \cos(n\phi - \phi_0))$				
Name	Dihedral	ϕ_0 (°)	k_{ϕ} (kJ/mol)	multiplicity
HOS _t /St	CH _n -CH-C _{ar} -CH _{ar}	0.0	4.184	2

Ryckaert-Bellemans Dihedrals $V_{rb}(\phi_{ijkl}) = \sum_{n=0}^3 C_n(\cos(\phi - 180^\circ))^n$					
Name	Dihedral	c_0 (kJ/mol)	c_1 (kJ/mol)	c_2 (kJ/mol)	c_3 (kJ/mol)
Backbone	CH _n -CH-CH ₂ -CH	8.397	16.785	1.134	-26.316

Fourier Dihedrals $V_F(\phi_{ijkl}) = \frac{1}{2}[C_1(1 + \cos(\phi)) + C_2(1 - \cos(2\phi)) + C_3(1 + \cos(3\phi)) + C_4(1 - \cos(4\phi))]$					
Name	Dihedral	c_1 (kJ/mol)	c_2 (kJ/mol)	c_3 (kJ/mol)	c_4 (kJ/mol)
HOS _t	CH _{ar} -C _{ar} -O-H	10.48	26.0	0.0	0.0
tBA/AA	CH ₂ -CH-C=O	10.48	26.0	0.0	0.0
tBA	CH-C-O-C	6.941	22.833	0.502	0.000
tBA	C-O-C-CH ₃	-12.501	8.962	-0.367	0.853

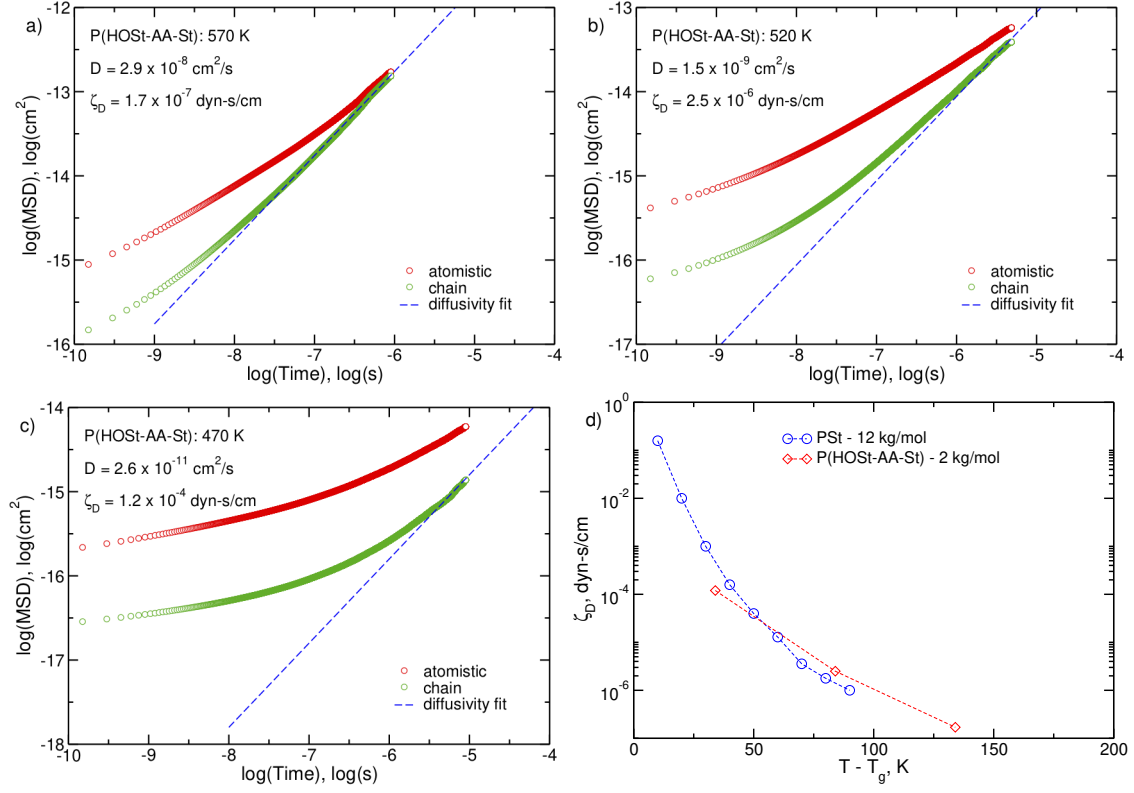


Figure A.3: Atom and chain center of mass mean-square displacements of P(HOST-AA-St) with linear fits to extract the chain center of mass diffusivity as a function of temperature (values shown on plots). Calculated monomeric friction coefficients are also provided (based on Eq. A.1) and plotted as a function of temperature (relative to glass transition recorded by experiments). Monomeric friction coefficients for 12 kg/mol polystyrene are also provided.

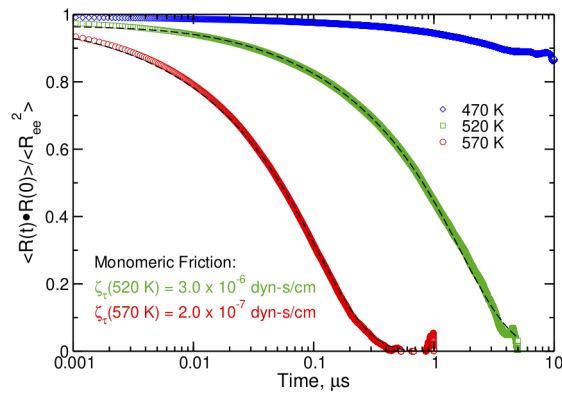


Figure A.4: End-to-end vector autocorrelation, normalized by the mean square end-to-end distance, of P(HOST-AA-St) as a function of temperature. Rouse fits for 520 and 570 K along with the extracted monomeric friction coefficients are provided.

transitions (for polystyrene and our system) as an independent variable. Eq. A.1 presumes the applicability of the Rouse model and it's relation for the end-to-end autocorrelation:

$$\langle R(t) \cdot R(0) \rangle = Nb^2 \sum_{p=1,3,5,\dots} \frac{8}{\pi^2 p^2} \exp\left(-\frac{tp^2}{\tau_1}\right) \quad (\text{A.2})$$

where b is the statistical segment length, p is the Rouse mode, t is time, τ_1 is the Rouse time (slowest relaxation mode), and $\langle R(t) \cdot R(0) \rangle$ is the end-to-end vector autocorrelation. Figure A.4 provides the end-to-end vector autocorrelation of polymer chains and the corresponding Rouse description which appears satisfactory. Monomeric friction coefficients can also be extracted as:

$$\zeta_\tau = 3\pi^2 \frac{k_B T}{N \langle R_{ee}^2 \rangle} \tau_1 \quad (\text{A.3})$$

where $\langle R_{ee}^2 \rangle$ is the mean square end-to-end distance, and ζ_τ is the monomeric friction coefficient. The values extracted at the two higher temperatures (where sufficient decorrelation was observed) are included in Figure A.4 and are in good agreement with previous estimates supporting further the Rouse description. Note that relaxation of the end-to-end vector has not been reached within the time simulated at 470 K. While we believe that this is not necessarily a requirement for sampling Na^+TFL^- diffusion (which decouples from polymer atomic displacements over the course of our simulation), 470 K was the lowest temperature we attempted to study with an initial configuration received from the 10 K/ns quenching.

A.5 Solvent removal from films

Solvent removal was performed at 403 K for 4 mins for all reaction samples following the procedure of our previous work. In our bilayer samples, since the diffusion layer on the stamp is not allowed to cool before stamping, we found a solvent removal bake of 383 K for 6 mins to provide a sharper interface between the diffusion and feeder layers while still being sufficient to remove both PGMEA and ethyl acetate from the respective layers. Figure A.5

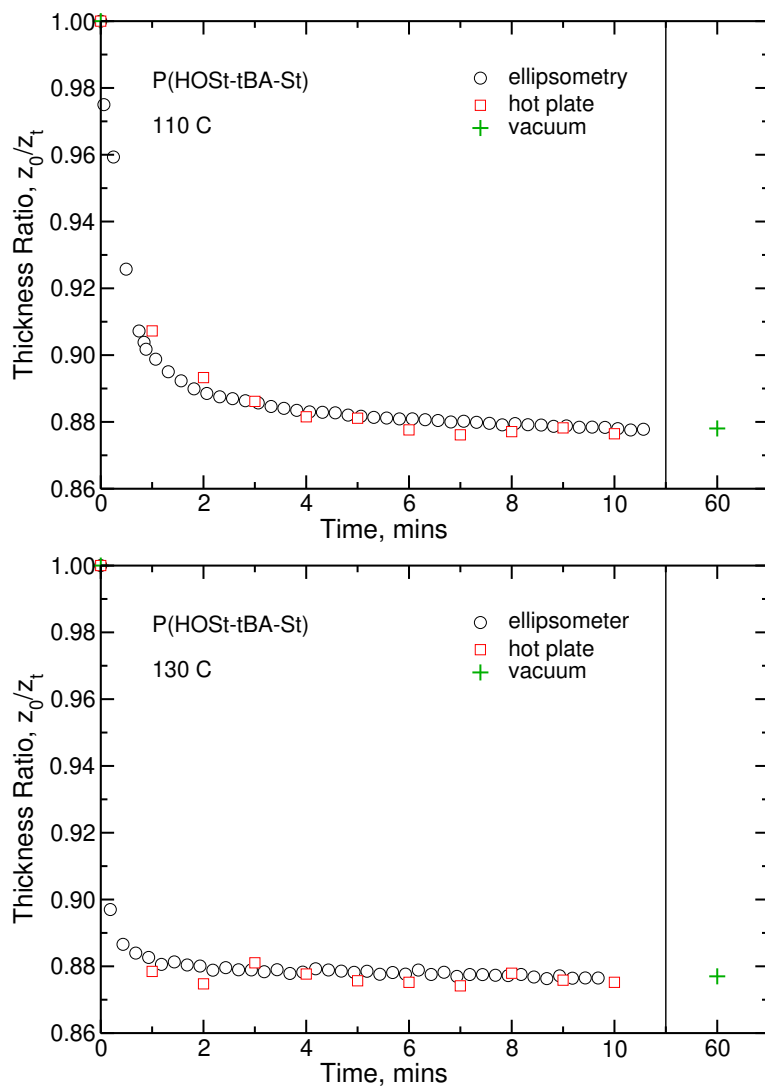


Figure A.5: Thickness ratio as a function of time for the three sample collection methods for P(HOSt-tBA-St) at baking temperatures of 383K (left) and 403 K (right). Loss of thickness is attributed to the removal of PGMEA. The x-axes are broken to show the long-time thickness ratio from the bake under vacuum.

provides data for PGMEA removal at 110 and 403 K as a function of time. Ethyl acetate removal is faster than PGMEA removal due to its higher vapor pressure. Data is collected in the form of the ratio of: the thickness as a function of time to the initial thickness of the sample, as the removal of solvent can be observed through the shrinkage of the film. 3 different techniques are used to track thickness as a function of temperature and time: 1) Through continuous baking of the sample on the ellipsometer heatcell. 2) A series of bakes on a hotplate (the same one used for solvent removal and sample preparation) at 1 minute intervals with the sample allowed to cool to room temperature between bakes before thickness collection. 3) Baking under vacuum for 60 mins. The samples used were prepared from a solution containing 8 wt% P(HOSt-tBA-St) in PGMEA which was spin-coated onto a silicon wafer at 2000 rpm and produces a thickness of approximately 250 nm after solvent removal. After 6 minutes for 383 K and 4 mins for 403 K, the thickness ratio for the ellipsometer and hot plate methods are approximately the same as the vacuum baked samples. Therefore, we believe that any remaining solvent in the films was negligible.

A.6 Atomic force microscopy (AFM)

AFM was performed using an Asylum MFP-3D Atomic Force Microscope. The topography and phase contrast were measured by scanning in tapping mode. The probes were silicon with a spring constant of approximately 9 N/m and a resonance frequency of 115 kHz. The parameters used for image acquisition were 0.8 Hz scan frequency, 20 μm x 20 μm scan size, and 256 $\times$ 256 image resolution. Raw AFM data were processed using the software provided by Asylum Instruments. First-order flattening was used to process both height and phase images. This eliminates any z offsets formed between scan lines by subtracting each point in the scan line with an average z value (z = phase or height). Solvent annealing in an atmosphere of ethyl acetate was used to remove large peaks and valleys (Figure A.6b) in topography of the polymer films on the poly(dimethyl siloxane) after spincoating. This creates a smooth film interface (Figure A.6c) for stamping onto the feeder layer. Final roughness of all interfaces are estimated to be < 5 nm.

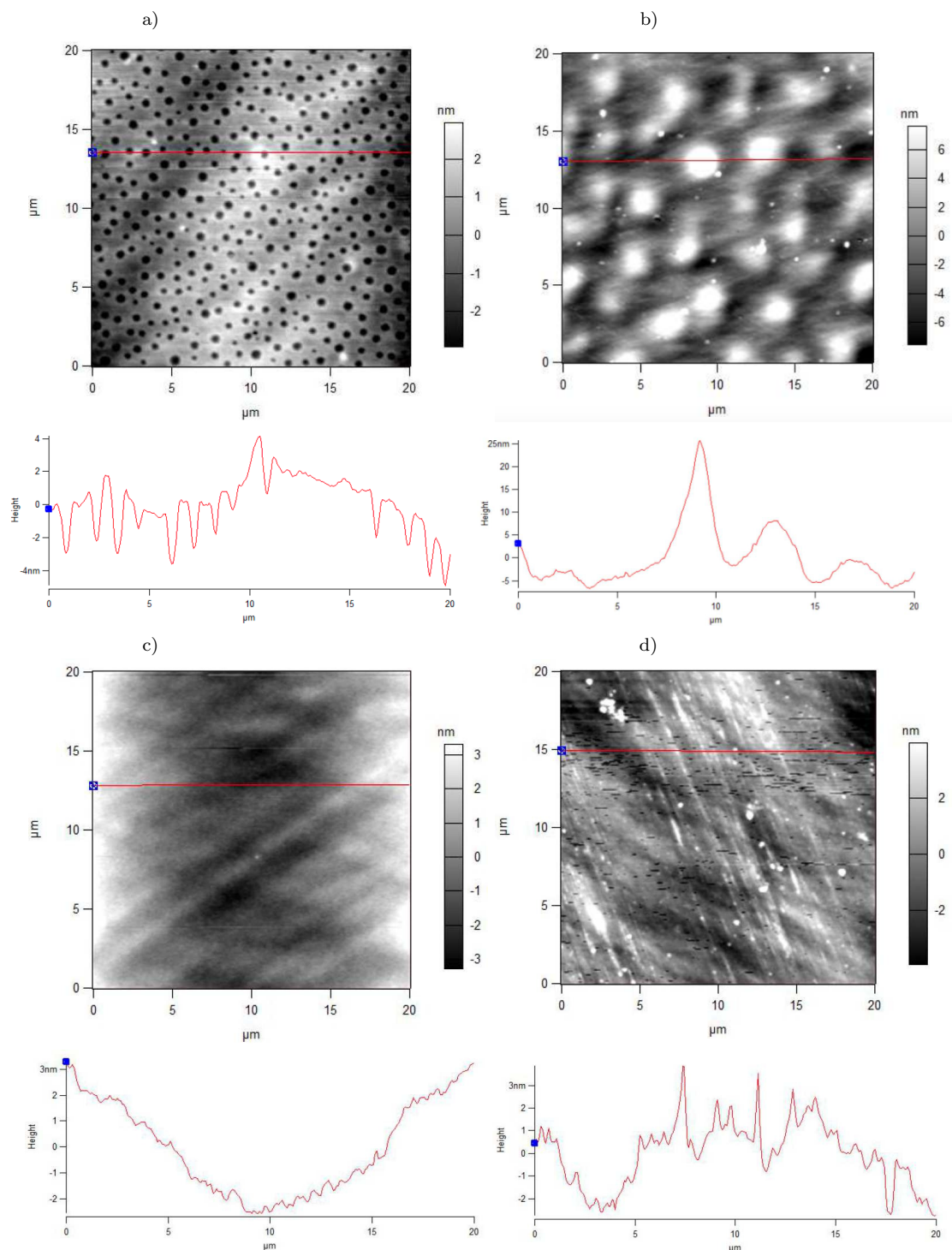


Figure A.6: AFM images and cross-sectional profiles for analysis of roughness at interfaces during bilayer building. a) The PDMS stamp used for transferring the diffusion layer onto the feeder layer. b) P(HOST-tBA-St) on the PDMS stamp before solvent annealing. c) P(HOST-tBA-St) on the PDMS stamp after solvent annealing. d) The free surface of the bilayer after stamping. Images, except for the pre-solvent annealed film, show very low roughness on the order of a few nanometers.

A.7 TOF-SIMS Na^+TFL^- calibration

TOF-SIMS data were calibrated through the use of the calibration curve provided in Figure A.7. The calibration curve was obtained from films of P(HOSt-tBA-St) and P(HOSt-AA-St) with known concentrations of Na^+TFL^- and thicknesses of approximately 300 nm. The relative ion counts for fluorine and an ionic fragment of PHOSt were determined from the bulk of the samples, at approximately 50 nm from the surface, and were found to have good linear agreement with the known number density of TFL^- .

A.8 TOF-SIMS profiles and fits

The initial concentration profile was modeled with a step function consisting of the known concentration of the feeder layer for all z from the known silicon interface depth to the known bilayer interface depth. Control samples obtained from cutting the bilayer samples prior to diffusion bakes were fit with this step function profile convolved with a Gaussian resolution function to determine an experimental resolution in the form of the standard deviation of the Gaussian distribution. For all samples this resolution was found to be roughly 20 nm. Diffusion baked sample data were modeled by integrating Fick's second law with the finite differences method. This method was defined over the 1-dimensional spatial (z) and time (t) domains with a spatial discretization of 1 nm and a time discretization that was adjusted to the diffusivity to maintain efficiency and stability, for example these values were 0.06 seconds for a diffusivity of $1 \times 10^{-14} \text{ cm}^2/\text{s}$ and 60 seconds for a diffusivity of $1 \times 10^{-17} \text{ cm}^2/\text{s}$. The finite differences method was performed until the bake time was reached and the final concentration profile was convolved with the optimized Gaussian resolution function determined from the control sample. The convolved profile was compared to the experimental data to determine residuals for optimization. Parameters for optimization were the diffusivity and the concentration of feeder layer step function bounded within 10% of the expected concentration as there can be small variations in the exact concentration from sample to sample. Sample data and fits are provided as a function of temperature, bake time, and concentration for P(HOSt-tBA-St) in Figure A.8 and P(HOSt-AA-St) in Figure A.9.

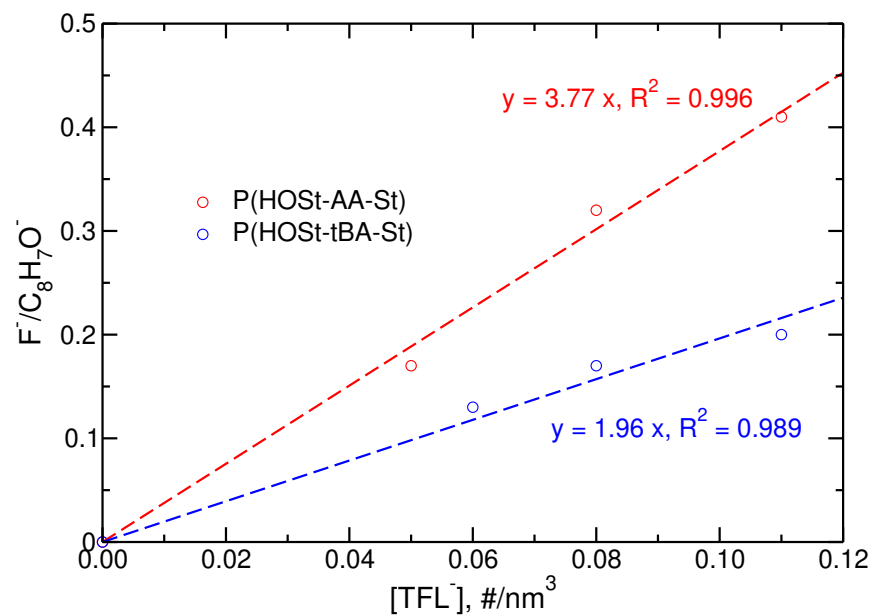


Figure A.7: Counts of fluorine ions normalized to counts of the PHOSt fragment. Data show good linear agreement, in which the slope varies with chemistry, with the number density of triflate ions in the calibration samples.

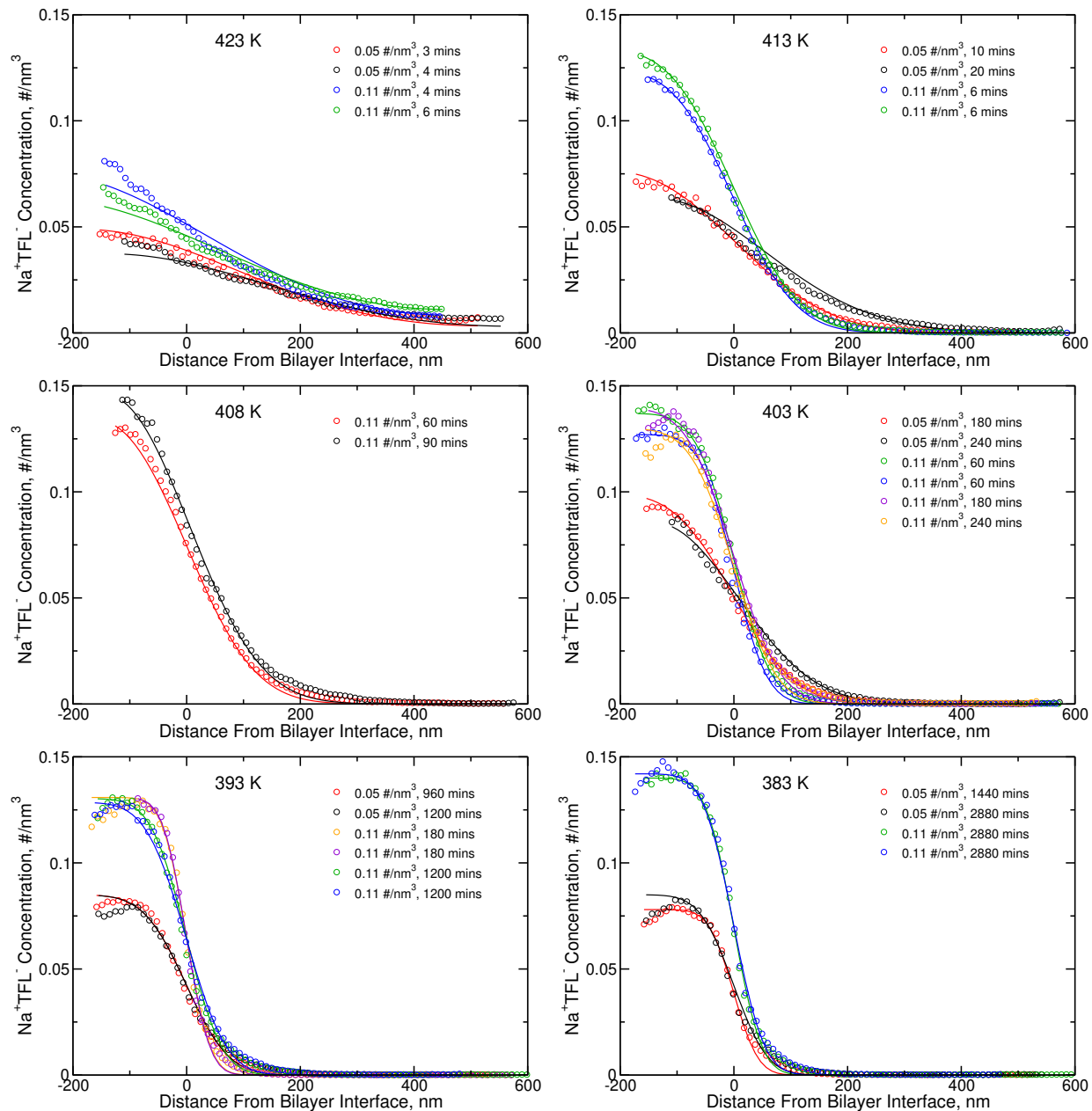


Figure A.8: Na⁺TFL⁻ concentration as a function of depth for P(HOSt-tBA-St). Each plot contains profiles as a function of feeder layer Na⁺TFL⁻ concentration and baking time for a specific temperature.

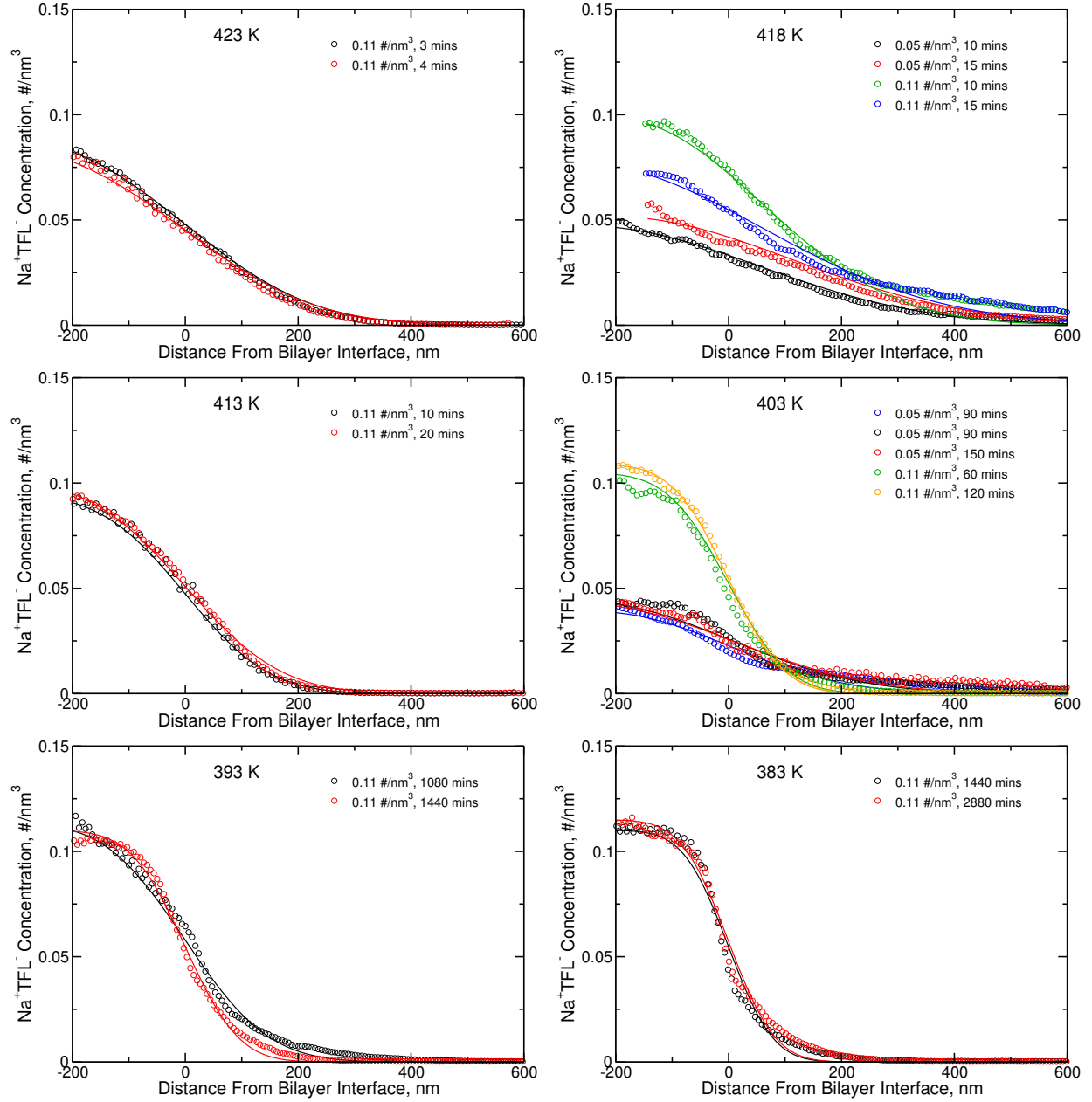


Figure A.9: Na⁺TFL⁻ concentration as a function of depth for P(HOSt-AA-St). Each plot contains profiles as a function of feeder layer Na⁺TFL⁻ concentration and baking time for a specific temperature.

A.9 KMC model of simulation with material relaxation

Figure A.10 provides the best-fit KMC models of transient local diffusion states for simulations with material relaxation at 520 K with dispersed $0.05 \text{ \#}/\text{nm}^3 \text{ Na}^+\text{TFL}^-$, at 520 K with equilibrium clustered $0.11 \text{ \#}/\text{nm}^3 \text{ Na}^+\text{TFL}^-$, and 470 K with equilibrium clustered $0.11 \text{ \#}/\text{nm}^3 \text{ Na}^+\text{TFL}^-$. The optimized parameters of the models are also provided.

A.10 KMC model of experiments

Figure A.11 provides the optimized parameters for best-fit KMC models of transient local diffusion states assuming no clustering for experiments at 350, 345, 340, and 335 K with 0.05, 0.08, and $0.11 \text{ \#}/\text{nm}^3 \text{ H}^+\text{TFL}^-$. Each temperature and catalyst concentration pair were fit individually to obtain these parameters.

Figure A.12 provides all experimental reaction kinetics data for 0.05, 0.08, and $0.11 \text{ \#}/\text{nm}^3 \text{ H}^+\text{TFL}^-$ at 350, 345, 340, and 335 K. Best-fit KMC model of transient local diffusion states with clustering are shown and numeric values of optimized parameters are provided.

A.11 Segmental dynamics of polymers

An approximation of the segmental dynamics of our polymer systems is found using the autocorrelation of the first Legendre polynomial ($P_1(\tau)$)[94] of the vector between the COM of the phenyl rings and the attached backbone carbon in HOSt repeat units, excluding end groups. Figure A.13 provides a comparison of this autocorrelation in equilibrium simulations of $0.11 \text{ \#}/\text{nm}^3 \text{ Na}^+\text{TFL}^-$ in the protected and deprotected polymers. Faster segmental dynamics are observed in the protected polymer. This is attributed to decreased hydrogen bonding and density in the protected polymer compared to the deprotected polymer.

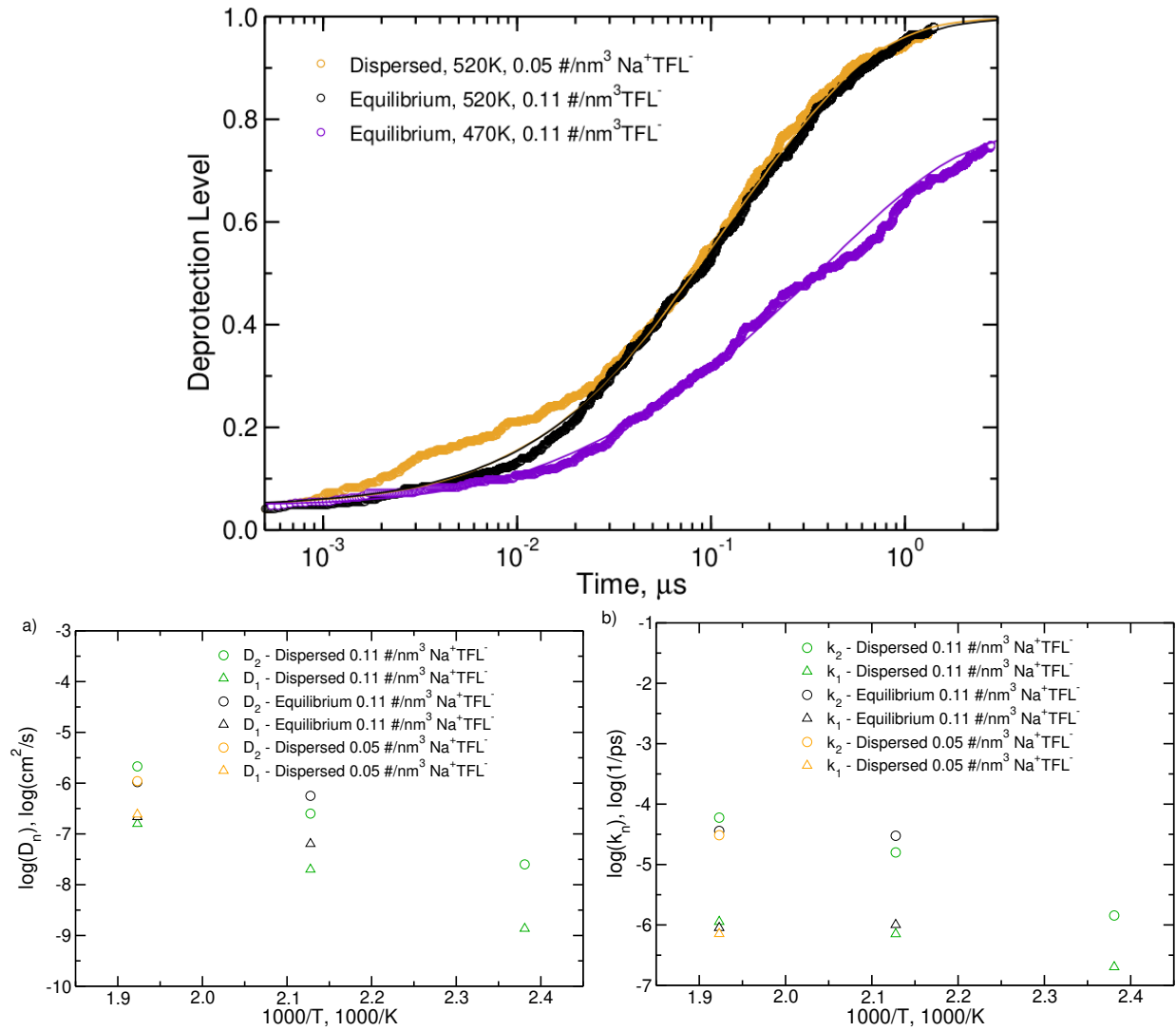


Figure A.10: (Top) Deprotection level (symbols) for simulations with material relaxation at 520 K with dispersed $0.05 \text{ \#}/\text{nm}^3 \text{ Na}^+\text{TFL}^-$, at 520 K with equilibrium clustered $0.11 \text{ \#}/\text{nm}^3 \text{ Na}^+\text{TFL}^-$, and 470 K with equilibrium clustered $0.11 \text{ \#}/\text{nm}^3 \text{ Na}^+\text{TFL}^-$. Best-fit KMC models of transient diffusivities (lines) are provided. (a) Temperature dependence of diffusivities (symbols) for all simulation with material relaxation conditions are provided. (b) Temperature dependence of transition rates (symbols) for all simulation with material relaxation conditions are provided.

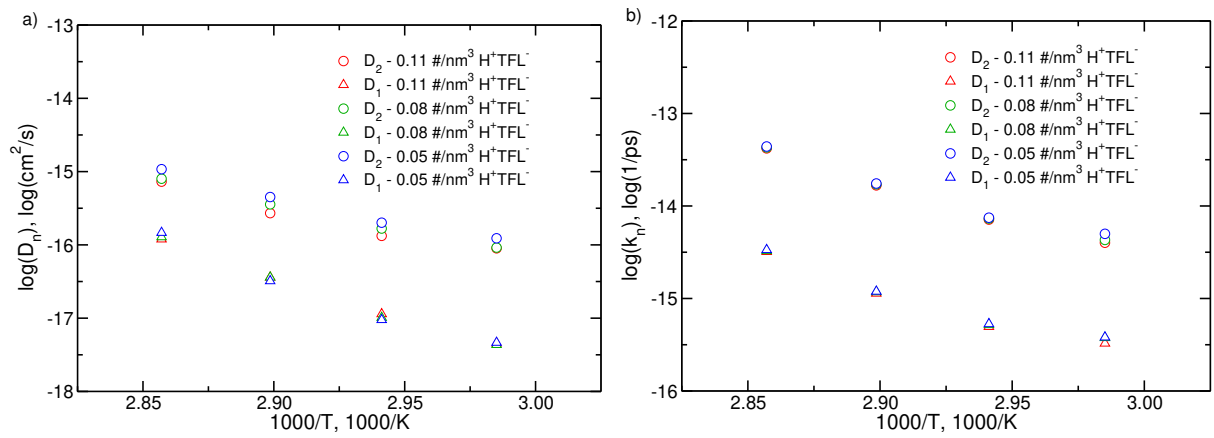


Figure A.11: (a) Temperature and concentration dependence of diffusivities (symbols) for all individually fit experimental reaction kinetics conditions. (b) Temperature dependence of transition rates (symbols) for all individually fit experimental reaction kinetics conditions.

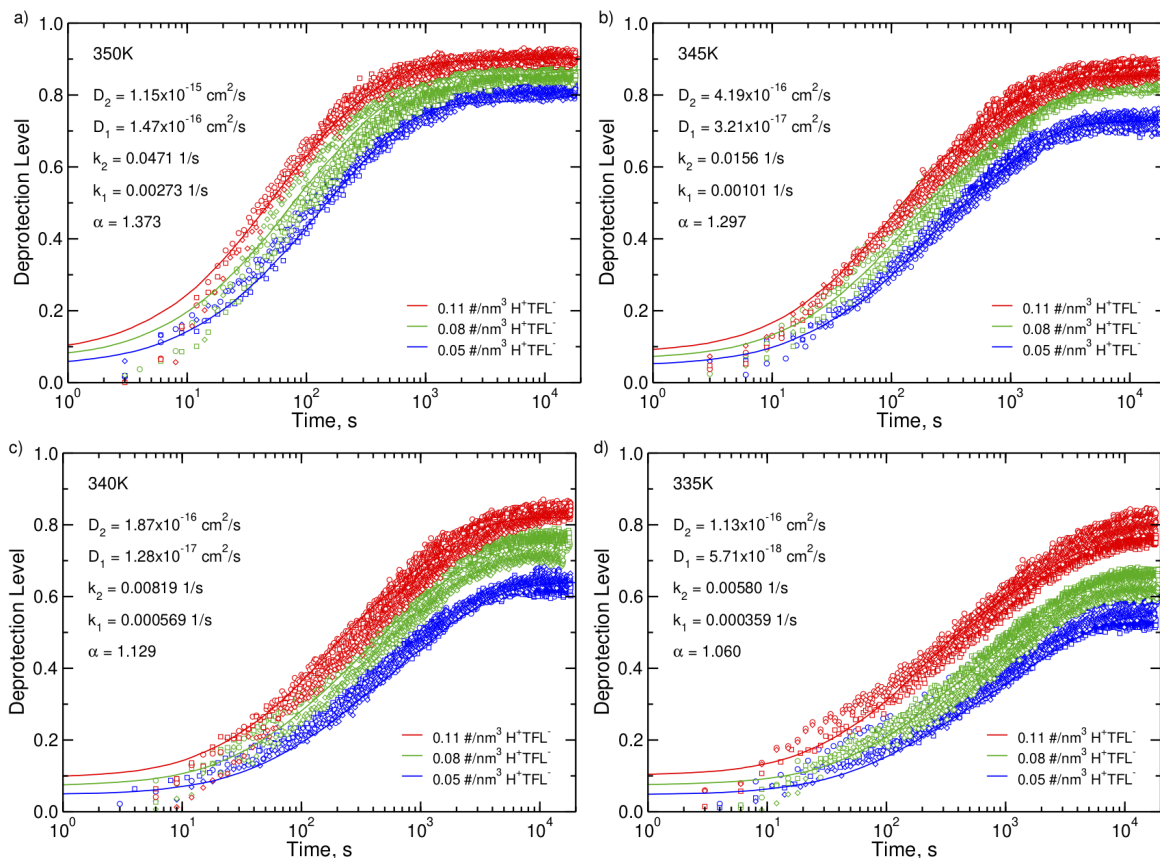


Figure A.12: (a) Deprotection level (symbols) for experimental reaction kinetics 350 K with 0.05, 0.08, and 0.11 $\#/\text{nm}^3$ H^+TFL^- fit simultaneously using the model concentration dependence based on catalyst clustering. (b) The same for 345 K. (c) The same for 340 K. (d) The same for 335 K. Best-fit KMC models of transient diffusivities (lines) and parameters for all conditions are provided.

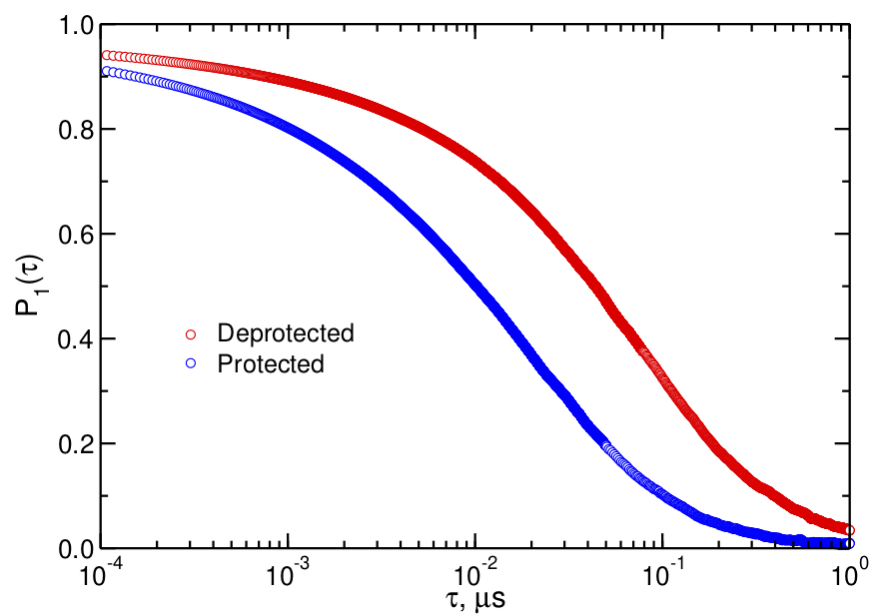


Figure A.13: Segmental dynamics of the polymer during equilibrium simulations of $0.11 \text{ \AA}^3/\text{nm}^3 \text{ Na}^+\text{TFL}^-$ in the protected and deprotected polymers.

Products of Dissertation

Refereed Journal Articles

- Bottoms, C. M.; Terlier, T.; Stein, G. E.; Doxastakis, M. Ion diffusion in chemically amplified resists. *Macromolecules* 2021, 54, 1912–1925, DOI: 10.1021/acs.macromol.0c02052.
- Bottoms, C. M.; Stein, G. E.; Doxastakis, M. Transient diffusion states during reaction in chemically amplified resists. 2022 Manuscript submitted for publication in special issue of *Journal of Physical Chemistry A*.
- Bottoms, C. M.; Stein, G. E.; Doxastakis, M. Counter-anion chemistry and reaction byproducts impact catalyst diffusion in chemically amplified resists. 2022 Manuscript in preparation.
- Bottoms, C. M.; Terlier, T.; Stein, G. E.; Doxastakis, M. Direct measurement of reaction and catalyst diffusion fronts in chemically amplified resists. 2022 Manuscript in preparation.

Refereed Conference Proceedings

- Bottoms, C. M.; Terlier, T.; Stein, G. E.; Doxastakis, M. Probing ion diffusion in chemically amplified resists through experiments and atomistic simulations. *Proceedings of The Society for Optics and Photonics. Advances in Patterning Materials and Processes XXXVIII* 2021, 11612, 37-48, DOI: 10.1117/12.2581367

- Bottoms, C. M.; Terlier, T.; Stein, G. E.; Doxastakis, M. Enhanced catalyst mobility in chemically amplified resists. Proceedings of The Society for Optics and Photonics. Advances in Patterning Materials and Processes XXXIV 2022 (Accepted)

Presentations

- Bottoms, C. M. Reaction-diffusion processes in chemically amplified photoresists. American Institute of Chemical Engineers Knoxville-Oak Ridge Section October 2018 Meeting: Poster.
- Bottoms, C. M. Ion diffusion in chemically amplified photoresists. Southeast Polymer Forum July 2019: Poster.
- Bottoms, C. M. Ion diffusion in chemically amplified photoresists. Applied Polymer Technology Extension Consortium 8th Annual Research Symposium November 2020: Poster.
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Vita

Chris is originally from Madison, North Carolina. He graduated from Wake Forest University with a B.S. in Chemistry with a concentration in Materials Chemistry in the Spring of 2016. While at WFU, he performed research in the materials science research group of Dr. Scott Geyer. He started the PhD program at the University of Tennessee in the Fall of 2016 and joined the polymers research groups of Dr. Gila Stein and Dr. Manolis Doxastakis. After completion of his PhD, expected in the Spring of 2022, he plans to continue to apply his broad materials science, engineering, experimental, and computational experience in the industrial research and development environment.