

Abstract Submitted  
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**Anomalous Kinetics in Reactive Polymer Glasses** GILA STEIN,

University of Houston — Image formation in modern lithographic processes is based on the acid-catalyzed deprotection of glassy polymer films. It is well-established that slow acid diffusion controls the reaction kinetics, but models based on Fickian transport coupled with a first-order reaction cannot describe experimental data. We studied the acid-catalyzed deprotection of glassy poly(hydroxystyrene-co-tertbutyl acrylate) films using infrared absorbance spectroscopy and stochastic simulations. Experimental data were interpreted with a model that explicitly accounts for acid transport, where heterogeneities at local length scales are introduced through a non-exponential distribution of waiting times between successive hopping events. Subdiffusive behavior predicts key attributes of the observed deprotection rates, such as fast reaction at short times, slow reaction at long times, and a non-linear dependence on acid loading. This transport model is consistent with other literature studies of probe diffusion in inert glasses. We highlight the complex behavior in photoresists by changing the size of acid-counterion pairs, incorporating plasticizer, and reducing film thickness. These data can facilitate the development of predictive lithography models that reflect the behavior of confined polymers.

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