Mechanistic Modeling of Epoxy Reaction Barriers using Network Descriptors

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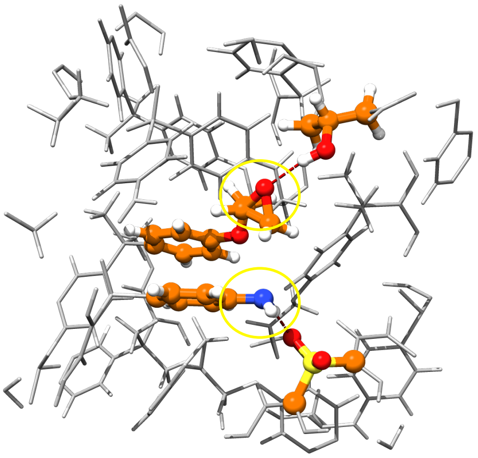

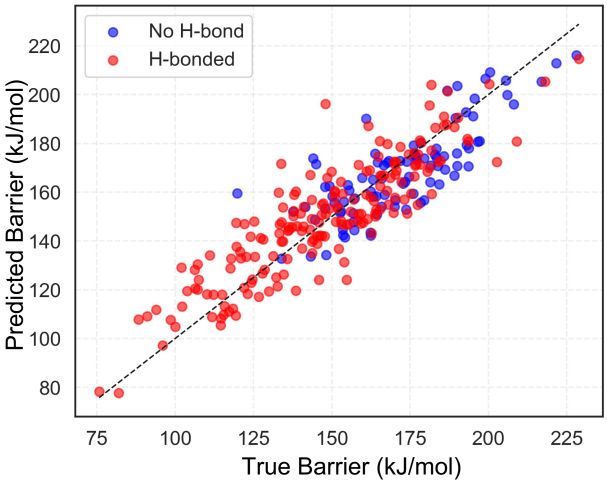

The curing of thermosets is governed by a complex interplay between local reaction geometry and the evolving covalent network. While simplified models capture qualitative trends in activation energies, they do not resolve how the environmental constraints imposed by the forming polymer network alter reaction kinetics under realistic curing conditions.

In our earlier QM/MM study of DGEBA/DDS systems [1], we quantified how hydrogen bonding modulates activation barriers. Building on this foundation, we extend these insights toward predictive curing simulations by coupling reactive molecular dynamics with QM/MM ONIOM transition-state analyses. Reactive configurations are extracted directly from in silico curing trajectories, enabling activation barriers to be computed within their polymer environment. This analysis reveals that the evolving network strongly modulates reaction energetics: hydrogen bonding, steric confinement, and geometric distortion together determine whether a reactive event remains energetically feasible as curing progresses.

From this mechanistic understanding, we identify a minimal, yet physically meaningful descriptor set capturing reactive-site geometry and hydrogen-bond contributions. These descriptors are evaluated against a large QM/MM barrier dataset to determine which structural features correlate robustly with activation energies across diverse network environments. Using this curated dataset, we train a supervised machine-learning model on ONIOM-derived barriers, enabling it to learn the mapping between local structural environment and activation energy.

Our ML model is deployed as an energy-aware reaction gate during reactive MD curing simulations. Candidate bond-formation events are evaluated on-the-fly, and only reactions predicted to be energetically feasible are allowed to proceed. Thus, network topology evolution is constrained by activation barriers learned from quantum-mechanical reference data rather than purely geometric proximity criteria. This framework links atomistic reaction energetics with network evolution and provides a scalable route toward energetically controlled in silico curing of thermosetting polymers.

[1] M. Livraghi, S. Pahi, P. Nowakowski, D. Smith, C.R. Wick, A.-S. Smith *The Journal of Physical Chemistry B*, **2023**, *127*, 7648-7662.