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Enhanced hydrogen bonding via epoxide-functionalization restricts mobility in poly(ethylenimine) for CO₂ capture†‡

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Free energy sampling, deep potential molecular dynamics, and characterizations provide insights into the impact of epoxide-functionalization on the hydrogen bonding and mobility of poly(ethylenimine), a promising CO₂ sorbent. These findings rationalize the anti-degradation effects of epoxide functionalization and open up new avenues for designing more durable CO₂ sorbents.

Effective technologies to reduce CO₂ emissions and atmospheric CO₂ levels are crucial in the fight against global warming and climate change. Carbon capture methods that use chemisorbents containing poly(ethylenimine) (PEI) show great promise as they are efficient in capturing CO₂ from flue-gas point sources or the atmosphere.^{1,2} However, PEI-based materials are known to undergo oxidative degradation, which causes a loss in CO₂ capacity after cycling.^{3,4} Overcoming this degradation will enable more rapid adoption of PEI-based sorbents for carbon capture and direct air capture.

Several recent studies have focused on improving the durability of PEI-based sorbents by exploring the potential benefits of epoxide-functionalization. For instance, Choi and Min *et al.* reported that functionalization of PEI supported in porous silica with 1,2-epoxybutane and epoxides with other side chains significantly improves its resistance to degradation under simulated wet flue gas conditions.^{5–7} Notably, this improvement

is especially pronounced when used in conjunction with chelators, effectively inhibiting the catalytic impact of ppm-level metal impurities. Taking a different approach, Hamdy *et al.* employed epoxy resin as the cross-linker to synthesize support-free cross-linked PEI, which demonstrated maintained CO₂ capacity throughout extensive aggressive adsorption/desorption cycles.⁸ Interestingly, epoxide-functionalization also enhances the oxidative stability of amine oligomers, such as tetraethylenepentamine.^{9,10} Min *et al.*^{11,12} and Guo *et al.*⁹ attribute the enhanced oxidative stability to changes in amine composition resulting from the conversion of primary amines to secondary amines through alkylation with hydroxyalkyl groups. However, contrasting findings have been reported, suggesting that amine stability cannot be solely attributed to amine identity.^{13,14} Another hypothesis suggests that abundant hydroxyl groups generated by epoxide-functionalization play a role in stabilizing amines through hydrogen bonding.^{11,12} However, the precise mechanism by which hydrogen bonding slows down amine oxidation remains largely unexplored.

The basic autoxidation scheme (BAS)¹⁵ in polymer degradation, involving radical reactions, may help explain the impact of hydrogen bonding on amine oxidation. As demonstrated by Rapoport *et al.*, the oxidative degradation rate of poly(propylene) is influenced by the mobility of amorphous chain segments, which impacts the rate of hydrogen abstraction responsible for radical propagation across polymer chains.¹⁶ Similarly, Denisov's review of literature reports on the oxidation kinetics of polymers concludes a strong correlation between polymer segmental mobility and the kinetics of radical reactions.¹⁷ Recent work by Colin *et al.* show that the rate constants of peroxy radical termination and propagation in epoxy-diamine networks can be controlled by modifying molecular mobility.¹⁸ Hydrogen bonding has been found to impact chain mobility in various polymer systems.^{19–21} Our previous studies on PEI and aminooligomers underscore the importance of radical reactions in degradation.^{14,22} These findings hint at potential connections between epoxide-functionalization, hydrogen bonding, polymer mobility, and degradation kinetics of amine sorbents.

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In BPEI and epoxide-functionalized BPEI, primary (1°), secondary (2°), and tertiary (3°) amines, as well as hydroxyl groups (OH) resulting from functionalization, have the potential to engage in hydrogen bonding networks. To quantitatively assess the strengths of these potential hydrogen bonds (H bonds), we use small molecules containing hydroxyl and/or amino groups as proxies (Fig. S1, ESI ‡) and compute the free energy profiles of intermolecular H bond acceptor-donor interactions using constrained *ab initio* molecular dynamics (AIMD) in conjunction with the blue-moon ensemble method. For further computational details, please refer to ESI ‡ , Section S1.1 and Fig. S2, S3.

The computed free energy profiles and bond free energies (ΔF) at 298 K for various H bonds are presented in Fig. 1. Among the amine-amine H bonds, only those involving a 2° amine as the donor exhibit shallow and elongated free energy wells, indicating weaker interactions. The remaining amine-amine H bonds have ΔF values greater than or equal to 0 kJ mol^{-1} , suggesting thermodynamically unfavorable interactions. In contrast, the H bonds involving OH as the donor display stronger interactions, with well-defined free energy wells and ΔF values ranging from -7 to -13 kJ mol^{-1} . Further simulations show that the H bond between a 1° amine and OH remains stable even at elevated temperatures (Fig. S4, ESI ‡), indicating its extended stability under typical CO_2 desorption and amine regeneration conditions. This stability is attributed to the small ΔS derived from the linear relationship between ΔF and temperature.

To investigate the hydrogen bonding environment in condensed-phase polymeric systems, we employ SCAN-trained deep potential molecular dynamics (DPMD) simulations²³ on liquid TETA, representing the oligomeric form of PEI. Within these simulations, a fraction of TETA molecules are replaced with functionalized TETA, where propylene oxide (PO) is attached to one of the 1° amine sites. Details regarding the simulation cell containing thousands of atoms, training of deep neural potentials, and DPMD parameters can be found in ESI ‡ , Section S1.2.



Fig. 1 Free energy profiles of nine examined hydrogen bonds involving amines and hydroxyl groups at 298 K. Bond free energies (ΔF), characterized as the energy of local minima at the bound states relative to the unbound states, are superimposed.

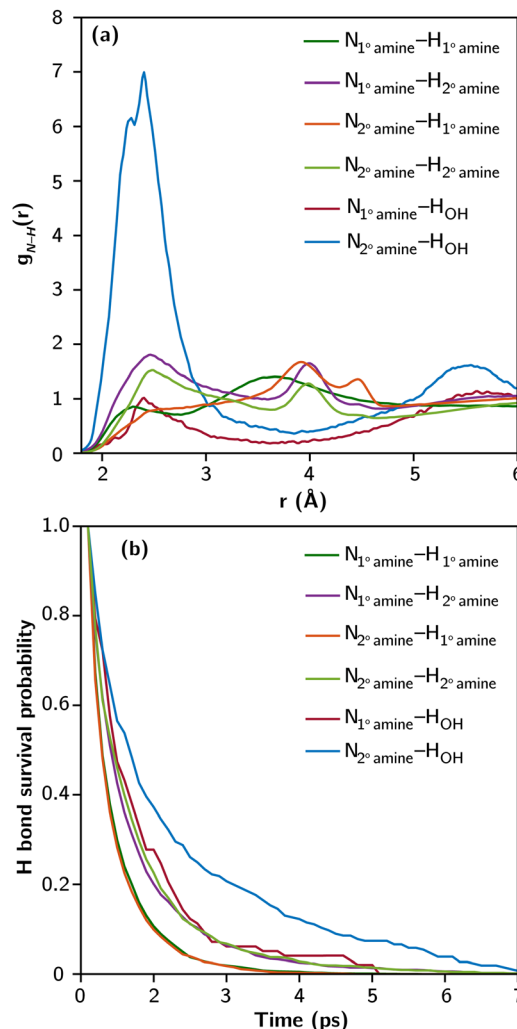


Fig. 2 (a) Partial radial distribution functions between N and H involving each type of N-H hydrogen bond potentially present in the partially PO-functionalized liquid TETA, and (b) their survival probability averaged over all hydrogen bonds of the same type from the DPMD trajectory.

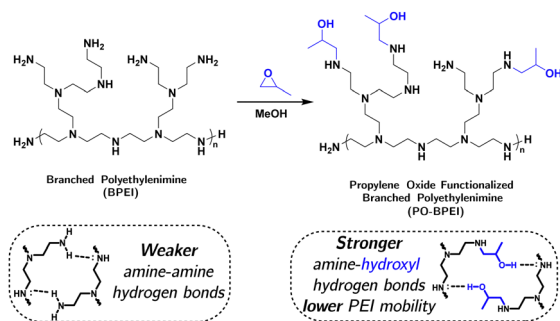
Fig. 2a presents the partial radial distribution functions between N and H ($g_{\text{N-H}}(r)$) of amines and OH groups based on 1.5 ns of DPMD trajectory. The range between 2 and 3 Å corresponds to the characteristic bond distance of N-H hydrogen bonds. The intensity and shape of the peaks vary across different N-H interactions. Notably, the peak associated with $\text{N}_{2^\circ} \text{ amine-HOH}$ is the strongest and sharpest, consistent with its highest bond strength (as shown in Fig. 1). The weak peak associated with $\text{N}_{1^\circ} \text{ amine-HOH}$ is due to the abundance of 2° amines and the prevalence of $\text{N}_{2^\circ} \text{ amine-HOH}$ hydrogen bonds, which utilize most of the available OH groups. Among N-H interactions involving only amines, those with $\text{N}_{2^\circ} \text{ amine}$ exhibit more prominent peaks than $\text{N}_{1^\circ} \text{ amine}$. Multiple peaks beyond 3 Å in the amine-amine $g_{\text{N-H}}(r)$ represent neighboring amines on the same TETA molecule.

The dynamics of hydrogen bonds were investigated by analyzing their survival probability, representing the history-dependent distribution of bond lifetimes. Fig. 2b shows the



We used ratiometric fluorescence to provide additional complementary mobility data for the three polymer samples across a wide range of temperatures, following our previous work.^{24,25} Tetrakis(4-hydroxyphenyl)ethylene (THPE) was employed as the fluorescent probe molecule in this work. THPE emits near 460 nm in a glassy matrix and 530 nm in a viscous solution

In summary, controlled simulations and characterizations provide strong evidence for the impact of epoxide-functionalization on reducing mobility in BPEL. The decreased mobility is attributed to robust hydrogen bonding interactions between hydroxyl functional groups and amines, supported by molecular simulations. Illustrated in Fig. 3, epoxide-functionalization



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Fig. 4 (a) DSC traces and estimated T_g values, (b) temperature dependence of the ratiometric fluorescence intensity (530 nm/460 nm) with 0.5 wt% THPE dissolved in, and (c) NMR relaxometry (T_1 and T_2) for BPEI, 0.2 O:N PO-BPEI, and 0.4 O:N PO-BPEI.

transforms primary amines into secondary amines with anchored alkyl tails containing hydroxyl groups, enabling more stable hydrogen bonding. The presence of stable hydrogen bonding restricts polymer chain mobility, slowing down the detrimental radical propagation reactions. However, polymer mobility is unlikely the sole factor influencing degradation kinetics, but becomes relevant in kinetic regimes where mobility-dependent reactions, like radical propagation, play a determining role.

The insights gained from these findings shed light on future sorbent design. To enhance stability, future research can explore methods to promote a more uniform distribution of hydroxyl groups in the polymer structure. Incorporating functional monomers during polymerization could facilitate this. Furthermore, incorporating functional groups with stronger hydrogen bond properties than hydroxyl groups, as well as exploring weak acid-base interactions with amines for increased stability without affecting CO₂ adsorption, are potential avenues for further investigation.

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Conflicts of interest

There are no conflicts to declare.

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