Distribution and Transport of CO₂ in Hydrated Hyperbranched Poly(ethylenimine) Membranes: A Molecular Dynamics Simulation Approach

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ABSTRACT: Hyperbranched poly(ethylenimine) (HB-PEI) has been distinguished as a promising candidate for carbon dioxide (CO₂) capture. In this study, we investigate the distribution and transport of CO₂ molecules in a HB-PEI membrane at various hydration levels using molecular dynamics (MD) simulations. For this, model structures consisting of amorphous HB-PEI membranes with CO₂ molecules are equilibrated at various hydration levels. Under dry conditions, the primary and secondary amines are highly associated with CO₂, indicating that they would participate in CO₂ capture via the carbamate formation mechanism. Under hydrated conditions, the pair correlations of CO₂ with the primary and secondary amines are reduced. This result suggests that the carbamate formation mechanism is less prevalent compared to dry conditions, which is also supported by CO₂ residence time analysis. However, in the presence of water molecules, it is found that the CO₂ molecules can be associated with both amine groups and water molecules, which would enable the tertiary amine as well as the primary and secondary amines to capture CO₂ molecules via the bicarbonate formation mechanism. Through our MD simulation results, the feasibilities of different CO₂ capture pathways in HB-PEI membranes are demonstrated at the molecular level.

1. INTRODUCTION
Excessive use of fossil fuels has been releasing large amounts of CO₂ and exacerbating global warming. The steady increase in the concentration of CO₂ in the atmosphere at 2.3 ppm per year over the past decade highlights the need to develop more efficient and effective mechanisms to capture CO₂ emissions. One solution is to mitigate the further worsening of the global greenhouse effect by restricting CO₂ emissions from fossil fuel-based power plants through carbon capture and sequestration. Unfortunately, this solution may require drastic process modifications, which could negatively impact plant productivity at many point sources. Additionally, this CO₂ emission mitigation strategy does nothing to address a century of previous CO₂ emissions.

An additional, complementary solution is the capture of CO₂ from ambient air. Direct air capture (DAC) of CO₂ produces an alternate complementary product: negative emissions. DAC can involve powered techniques including heating and cooling as well as passive adsorption and absorption techniques. Given the ratio of air to CO₂ molecules (2500:1), to capture a large amount of CO₂, very large volumes of air must be collected. Thus, powered air capture technologies that involve significant compression or refrigeration can be energy-intensive. These limitations render absorption and adsorption as the most commonly used DAC technologies. Both techniques are relatively energy-efficient and primarily require power during the sorbent regeneration process (CO₂ desorption), rendering them potentially cost-effective.

Among these techniques, the most popular ones include absorption with liquid amines or alkaline solutions and adsorption with solid amines. Absorption with liquid basic media presents several challenges such as high volatility (if amines are used) and high alkalinity, leading to corrosion and degradation issues and hindering overall performance. Another disadvantage of absorption is that use of aqueous media is energy-intensive because water, with its high heat capacity, must be heated to recover CO₂. As such, although absorption is a conventionally used method in modern industry for point source capture, these disadvantages highlight the opportunity to develop more efficient technologies.

Two remaining means of CO₂ capture involve solid adsorption and membranes. Of these, membranes are
especially advantageous due to a high concentration of amines that enhances their thermal stability, leading to a higher CO₂ capturing efficiency. Among these membranes, poly(ethyleneimine) (PEI) is particularly promising because of its low volatility and high amine density, thereby maximizing the benefits that can be obtained from use of solid sorbents to replace aqueous liquids. Specifically, branched PEI is favored over linear PEI due to its high available free volume and high primary-to-secondary amine ratio, both of which make this material favorable for CO₂ capture.

Previous studies have identified two dominant mechanisms of CO₂–amine reactions. Alkylammonium carbamate species form under both dry and humid conditions and involve reaction with either primary or secondary amines in solid sorbents. By contrast, the bicarbonate reaction can occur on amines of all types (primary, secondary, or tertiary) but requires the presence of water. Gaining further insights into the dominance of either mechanism under various hydration conditions would allow researchers to tailor the design of future solid sorbents and membranes for optimal scavenging in a given application.

Molecular dynamics (MD) simulations can offer useful insights into these systems due to their capacity to illuminate the local structures at a molecular level surrounding these amines to an extent beyond the capability of many current experimental methods. For example, Sharma et al. used MD simulations to determine which PEI nanostructures were conducive to CO₂ capture, observing that spacious regions and interfaces were most favorable and concluding that free volume and entropy are the most influential factors in predicting the effectiveness of a given PEI. Another MD simulation study by Shen and co-workers demonstrated the importance of decreasing chain length in order to increase CO₂ capture in low-molecular-weight PEI.

In this study, therefore, we investigate the distribution and transport of CO₂ in a HB-PEI membrane at various hydration levels using the MD simulation method. The details of the local structures and transport properties in the HB-PEI membranes are scrutinized to elucidate the CO₂ capture mechanisms in the membranes. From this study, we seek to make contributions to molecular design guidelines for new polymeric materials with desirable CO₂ capture properties.

2. RESULTS AND DISCUSSION

2.1. Structure of Hyperbranched PEI Membranes. A typical hydrated membrane consisting of hyperbranched poly(ethyleneimine) (HB-PEI, Figure 1) and 75 CO₂ molecules is presented in Figure 2, through which the primary, secondary, and tertiary amine groups are distributed evenly. Other models simulated using the conditions in Table 1 are not displayed here since they appear similar in this format of visualization. To quantitatively analyze the distribution of such amine groups, we used a pair correlation analysis for various pairs.

2.1.1. Amine–H₂O Pair Correlation. It is expected that the structure in the HB-PEI membrane would be affected by the extent of hydration because the water molecules would gather around the hydrophilic amine groups in the membrane. Therefore, to further investigate the effect of hydration on the HB-PEI membrane structure, particularly on the amine group distribution, we first analyzed how the amine groups are solvated by water molecules.

In Figure 3a, it is presented that the H₂O–H₂O pair correlation becomes stronger as a function of hydration. The enhanced ρ_{H₂O−H₂O}(r) at higher hydration indicates that the water molecules are segregated together in close proximity to form water clusters in HB-PEI membranes. The coordination numbers for water, CN_{H₂O}(H₂O), calculated from the first solvation shell (r < ~3.5 Å) are 2.53 at the low hydration level.
with 75 water molecules (∼0.04 g/cm³) and 3.82 at the high hydration level with 300 water molecules (∼0.13 g/cm³), as summarized in Table 2. Please note that such water molecules are associated with hydrophilic moieties in the membrane that are amine groups.

Indeed, Figure 3b,c exhibits that the amine groups are associated with more water molecules as the hydration increases for all amine types. Additionally, it is commonly observed under both hydration conditions that the extent of $\rho_{HN-H_2O}(r)$ is in the order of primary, secondary, and tertiary amines: 1N > 2N > 3N, where 1N, 2N, and 3N denote primary, secondary, and tertiary amines, respectively. Apparently, this is reflected in the water coordination number for each amine type. As also shown in Table 2, $CN_{H_2O}$ (1N) has the largest value due to the hydrogen bond formation capability of the primary amine group with water molecules, while $CN_{H_2O}$ (2N) and $CN_{H_2O}$ (3N) are 30–40% and 3–4.5% of $CN_{H_2O}$ (1N), respectively, indicating that the primary and secondary amine groups predominantly interact with water molecules.

### Table 2. Water Coordination Numbers for Water and Amine Groups

| number of CO2 | number of H₂O | CN$_{H_2O}$ (H₂O) | CN$_{H_2O}$ (1N) | CN$_{H_2O}$ (2N) | CN$_{H_2O}$ (3N) |
|--------------|---------------|--------------------|-----------------|-----------------|-----------------|
| 0            | 75            | 2.53               | 0.29            | 0.11            | 0.01            |
| 0            | 300           | 3.82               | 0.54            | 0.18            | 0.02            |
| 75           | 75            | 3.15               | 0.21            | 0.08            | 0.01            |
| 75           | 300           | 3.92               | 0.44            | 0.15            | 0.02            |

Figure 3. Pair correlation analysis for (a) water–water pair; (b) amine–water pairs at low hydration with 75 water molecules (∼0.04 g/cm³); and (c) amine–water pairs at high hydration with 300 water molecules (∼0.13 g/cm³).
shown in Figure 1, the primary amine groups are in close proximity to the secondary and tertiary amine groups separated by one ethylene moiety, whereas each primary amine group is far from other primary amine groups that are more than two ethylene moieties apart. Therefore, most of the short-range amine−amine pair correlations (r < ∼4.5 Å) are attributed to the covalent connection, implying that the longer-range amine−amine pair correlations likely involve primarily intermolecular amine−amine pair correlations.

The effect of hydration on the internal structures of HB-PEI membranes is analyzed using the amine−amine pair correlations, ρgN−N(r). Before conducting this analysis, we expected that ρgN−N(r) could be weakened and also shifted out in the amine−amine distance because each amine group could be solvated by water molecules. However, it is clearly shown in Figure 4 that each ρgN−N(r) remains nearly the same regardless of the variation of hydration. Why is ρgN−N(r) not affected by the hydration despite ρgH2O−H2O(r) and ρgN−H2O(r) being clearly enhanced, as shown in Figure 3? One possible answer for this question would be that the internal structure of HB-PEI membrane does not undergo noticeable changes up to 300 water molecules, implying that water molecules mainly tend to form a water cluster under this simulated condition rather than spreading throughout the membrane. Finally, it should be noted that when CO2 molecules are added and the hydration level is kept constant, ρgN−H2O(r) is decreased and ρgH2O−H2O(r) is increased. It is thought that the CO2 molecules tend to occupy the space around the amines and to exclude H2O molecules from the space surrounding the amines, thereby lowering ρgN−H2O(r). Consequently, such excluded water molecules might migrate to the aqueous region and associate with other water molecules, thereby increasing ρgH2O−H2O(r).

2.1.3. Amine−CO2 Pair Correlation. As confirmed from numerous studies, the primary and secondary amines can capture CO2 via (1) the carbamate formation mechanism in the presence or absence of H2O in close proximity and (2) the bicarbonate formation mechanism only in the presence of H2O. However, the tertiary amine can only participate in the bicarbonate formation mechanism because it has no hydrogen atom attached to the nitrogen atom.20−26

Figure 4. Pair correlation analysis for amine−amine pairs under various hydration conditions: (a) primary amine; (b) secondary amine; and (c) tertiary amine. The numbers in the parentheses of insets indicate the number of water molecules. The low and high hydration conditions correspond to ∼0.04 g/cm3 and ∼0.13 g/cm3, respectively. Seventy-five CO2 molecules correspond to ∼0.08 g/cm3.
CO₂ + 2R₂NH ↔ R₂NCO₂⁻ + R₂NH₂⁺  
(1)

CO₂ + R₂N + H₂O ↔ CO₂H⁻ + R₂NH⁺  
(2)

Since the CO₂–amine reactions require a close distance between amines and CO₂, we analyzed the amine–CO₂ pair correlation in the HB-PEI membrane under various hydration conditions, as demonstrated in Figure 5. Under the dry condition (0 H₂O, Figure 5a), it is found that ρ_SN–CO₂(r) has a strong peak at ~3.9 Å, meaning that CO₂ molecules are closely associated with the primary amine groups. The relatively short distance between the primary amine groups and surrounding CO₂ molecules is mediated by the hydrogen bonding interaction of the oxygen of CO₂ with the hydrogen of the primary amine group. Accordingly, ρ_SN–CO₂(r) has a weaker intensity than ρ_SN–CO₂(r) because the secondary amine group has lesser capability to interact with CO₂ molecules, likely due to steric hindrance as well as a lesser number of hydrogen atoms. Indeed, this explanation based on the hydrogen-bond-mediated amine–CO₂ correlation can be further applied to the tertiary amine, showing very weak correlation with CO₂.

Another point in Figure 5a is that the secondary and tertiary amines have a correlation with CO₂ at ~5.5 Å. Considering that even the tertiary amine groups have this correlation at ~5.5 Å without forming a direct hydrogen bonding interaction with CO₂, the correlation of the secondary and tertiary amines with the CO₂ molecules at ~5.5 Å should be an indirect correlation due to the direct correlation of CO₂ with primary and secondary amine. In other words, the CO₂ molecules in the vicinity of the primary and secondary amine groups at a distance of ~3.9 Å are also located nearby the tertiary amine groups at a distance of ~5.5 Å. Here, it should be noted that, despite the different proximity of the secondary and tertiary amines to the primary amines within the HB-PEI molecule, the branched PEI structure can bend such that secondary and tertiary amines are at a similar distance from the primary amine, and therefore, ρ_SN–CO₂(r) and ρ_SN–CO₂(r) show a similar trend regardless of the structural proximity to 1N.

We also analyzed the amine–CO₂ pair correlations in the presence of water molecules at 75 H₂O and 300 H₂O from Figure 5b,c, respectively. It is intriguing that the intensity of ρ_SN–CO₂(r) is reduced with increasing hydration, whereas ρ_SN–CO₂(r) and ρ_SN–CO₂(r) do not undergo significant changes. For a more quantitative analysis, the CO₂ coordination numbers for each amine type are summarized in Table 3. Indeed, CNCO₂ (1N) is noticeably decreased in the presence of water molecules (Table 2). This suggests that the CO₂ and H₂O molecules compete with each other to interact with the primary amine groups. In the case of the secondary amine, CNCO₂ (2N) is decreased, but the extent of change is very small, meaning that the competition around the secondary amine is weaker in comparison to the primary amine. In this context, the CO₂ molecules excluded from the primary and secondary amines due to the competition with water molecules are increasingly around the tertiary amine groups, showing a slight increase in CNCO₂ (3N), as presented in Table 3.

2.1.4. Other Pair Correlations. The CO₂–H₂O and CO₂–H₂O pair correlations are presented in Figure 6. As expected, ρ_SN–H₂O(r) increases with water content (Figure 6a). These additional water molecules available around CO₂ would facilitate bicarbonate formation since such water molecules would be also readily available around amine groups (Figure 3). In contrast, ρ_SN–CO₂(r) does not seem to be affected by the hydration level. This result suggests that CO₂ does not have a strong interaction with water molecules, which is consistent with the poor solubility of CO₂ in water. As such, ρ_SN–CO₂(r) is primarily determined by probabilistic chance as a function of the concentrations of CO₂ and water.

Table 3. CO₂ Coordination Numbers for Amine Groups

| number of H₂O | CNCO₂ (1N) | CNCO₂ (2N) | CNCO₂ (3N) |
|---------------|------------|------------|------------|
| 0             | 1.02       | 0.64       | 0.26       |
| 75            | 0.88       | 0.62       | 0.39       |
| 300           | 0.84       | 0.62       | 0.39       |

Figure 5. Pair correlation analysis for amine–CO₂ pairs under various hydration conditions: (a) 0 H₂O; (b) 75 H₂O; and (c) 300 H₂O. The low and high hydration conditions correspond to ~0.04 g/cm³ and ~0.13 g/cm³, respectively. Seventy-five CO₂ molecules correspond to ~0.08 g/cm³.
molecular transport of CO2 and H2O molecules was evaluated system (corresponding to rate since the CO2 molecules must make physical contact with Conditions participate in bicarbonate formation reactions with CO2. Thus, amine groups as well as the primary and secondary amines to adsorbent or membrane since water molecules enable tertiary CO2 di displacement (MSD) analysis during equilibrium MD simulations, as presented in Table 4.

Table 4. Diffusivity of CO2 and H2O under Dry and Humid Conditions

| number of CO2 | number of H2O | CO2 (×10^{-5} cm^2/s) | H2O (×10^{-5} cm^2/s) |
|---------------|---------------|------------------------|-----------------------|
| 5             | 0             | 0.673                  |                       |
| 75            | 0             | 1.847                  |                       |
| 75            | 75            | 1.695                  | 0.1608                |
| 75            | 300           | 1.449                  | 0.1491                |

First, under a very dilute condition of five CO2 molecules/system (corresponding to ~0.0049 g/cm^3), it is found that the CO2 diffusivity is lower than that under the 75 CO2 molecules/system condition (corresponding to ~0.08 g/cm^3). This is attributed to the more enhanced motions of the constituent molecules due to a high concentration of gaseous CO2 molecules. On the other hand, it is noted that the CO2 diffusivity is diminished with increasing water content: the CO2 diffusion coefficients are reduced by 8.2% and 21.5% at 75 H2O/system and 300 H2O/system compared to the dry condition, respectively. By assuming that the CO2 diffusion takes place via a hopping mechanism via free volume in the membranes, it is proposed that more water molecules occupy the free volume in the membrane as the water content is increased. To confirm this explanation, we investigated the free volume fraction, defined as the average available free volume normalized by the total system volume. Please note that the probe size was r = 1.65 Å, corresponding to the hydrodynamic radius of CO2. As summarized in Table 5, the free volume fraction trends with the diffusion coefficient. However, it should be stressed that not all the water molecules occupy the free volume in the membrane but rather form a separate water phase, inferring that the total system volume can be increased. Indeed, it is confirmed that the total system volume is increased as a function of hydration level, implying that the water content beyond a certain capacity of the membrane induce the formation of water phases.

Finally, to further understand the CO2 transport in the HB-PEI system, we calculated the average residence time of CO2 around amine groups, H2O around amine groups, and CO2 around H2O in our simulation systems. Please note that this study employed a classical MD simulation method, and the reaction between molecules cannot be directly described. Therefore, the CO2 residence time discussed here should be interpreted as the residence time of CO2 around amine wherein no reaction takes place. The residence time of CO2 around an amine group (CO2/N) is defined as the length of time that the carbon atom in CO2 spends within the first CO2 shell at a distance <4.09 Å from the amine groups. It should be noted that while CO2 molecules interact with primary, secondary, and tertiary amines in various first shell cutoff distances, the shortest cutoff (4.3 Å) was chosen to guarantee that all residence times represented first shell interactions. To obtain the mean residence time, the distances between CO2 molecules and amine groups were recorded over the last 2 ns of our simulations. Then, these distance trajectories were analyzed to count the number of events for CO2 staying within cutoff distance from the amine groups during a given amount of time, which were processed to determine the mean residence time. From Table 6, it is observed that the number of CO2 molecules has very little effect on the residence time. However, when water molecules are added, the residence time decreases by ~8.5%. This is consistent with the CO2−N pair

2.2. Transport of CO2 and H2O in Hyperbranched PEI Membranes. CO2 transport through the HB-PEI membrane is one of the critical properties to determine the CO2 capture rate since the CO2 molecules must make physical contact with the amine groups for reaction. Likewise, water transport is also a crucial governing factor for the CO2 capture capacity of the adsorbent or membrane since water molecules enable tertiary amine groups as well as the primary and secondary amines to participate in bicarbonate formation reactions with CO2. Thus, molecular transport of CO2 and H2O molecules was evaluated using diffusion coefficients calculated from the mean squared displacement (MSD) analysis during equilibrium MD simulations, as presented in Table 4.

Table 5. Average Free Volume Fraction under Dry and Humid Conditions

| number of CO2 | number of H2O | free volume fraction | total volume (Å^3) |
|---------------|---------------|----------------------|--------------------|
| 5             | 0             | 0.401                | 60291.90           |
| 75            | 0             | 0.417                | 65853.85           |
| 75            | 75            | 0.412                | 68438.82           |
| 75            | 300           | 0.408                | 74758.49           |

Table 6. Average Residence Time (in ps) of CO2 around Amine, H2O around Amine, and CO2 around H2O under Dry and Humid Conditions

| number of CO2 | number of H2O | CO2/N | H2O/N | CO2/H2O |
|---------------|---------------|-------|-------|---------|
| 5             | 0             | 12.41 |       |         |
| 75            | 0             | 13.01 |       |         |
| 75            | 75            | 11.90 | 17.79 | 13.45   |
| 75            | 300           | 11.91 | 18.09 | 15.00   |
correlations in Figure S, wherein the addition of water lowers this CO$_2$–N pair correlation. Intriguingly, further addition of water molecules has no significant effect upon the residence time, again consistent with the pair correlations in Figure S.

Next, we analyzed the residence time of H$_2$O around amine groups (H$_2$O/N, cutoff distance = 3.59 Å) and that of CO$_2$ around H$_2$O (CO$_2$/H$_2$O, cutoff distance = 4.65 Å). Consistent with our observations of a decreasing H$_2$O diffusion coefficient with increasing hydration, these residence time values increased with water content. This is potentially because higher hydration provides more opportunity for favorable interactions between H$_2$O, CO$_2$, and amine group (i.e., longer residence time). This could also indicate that higher water contents are more conducive to CO$_2$ capture via the bicarbonate mechanism.

A population analysis of residence time data is presented in Figure 7. From this, we can surmise information regarding the extent of pair interactions in various systems. It appears that the most common interactions are between CO$_2$ and N, with the frequency of this interaction being decreased slightly in the presence of water (presumably due to the competition of CO$_2$ with water for amine groups). Interaction between water and N is the next most frequent interaction. Intriguingly, despite longer average residence times, the frequency of this interaction is actually decreased when water content is increased. This is likely due to the lower H$_2$O diffusion coefficient. At higher water contents, H$_2$O is less dynamic and its interactions with amines tend to be less frequent with longer residence time. Finally, the interactions between water and CO$_2$ are the least frequent in all systems, presumably due to their weak interaction as known from the poor CO$_2$ solubility with respect to water.

3. CONCLUSIONS

The purpose of this study was to characterize the distribution and transport of CO$_2$ molecules in dry and hydrated HB-PEI. Under dry conditions, both primary and secondary amines showed strong association with CO$_2$, indicating potential for the carbamate formation mechanism. Under hydrated conditions, such CO$_2$ association with the primary and secondary amines decreased because water molecules compete with the CO$_2$ molecules, suggesting that carbamate formation activity would be decreased in the presence of water molecules. Analyses of coordination numbers and residence times confirm the phenomenon of CO$_2$ exclusion from primary and secondary amines due to the addition of water. Intriguingly, CO$_2$ mobility is also decreased as a function of hydration due to diminished free volume within the membrane. It should be noted that the association between water, CO$_2$, and tertiary amines could indicate potential for the bicarbonate formation mechanism under hydrated conditions, but this association effect is generally small.

From our MD simulations, it was confirmed at a molecular level that the amine groups of HB-PEI associate with both CO$_2$ and water molecules. Considering that the classical MD simulation cannot directly describe the chemical reactions in carbamate and bicarbonate formations, it is noted that further effort is required to develop methods to describe the reactions in order to elucidate the cooperation or competition among CO$_2$ and water molecules in the vicinity of the amine groups.

4. MODELING AND COMPUTATIONAL DETAILS

4.1. Preparation of the Simulation Cell. HB-PEI atomistic monomer structures were created using Cerius$^2$, as presented in Figure 1, wherein the ratio of primary to secondary to tertiary amines was maintained at 6:5:4 (fitted to reproduce the NMR observation (42/33/25) and a molecular weight of 764.3). The monomer structures were geometrically optimized using a density functional theory (DFT) method with B3LYP and 6-31G** in Jaguar. Charges were then calculated on each atom using a Mulliken population analysis. These DFT charges are assigned to atoms within the structure and used in subsequent MD simulations.

The 3D periodic, amphorous simulation cells were constructed as shown in Figure 2 using Monte Carlo techniques by cloning various concentrations of CO$_2$, HB-PEI, and water, as summarized in Table 1. In detail, condition 1 has only an HB-PEI membrane without CO$_2$ and water molecules, and its main purpose is to characterize the distribution of primary, secondary, and tertiary amines in the membrane; conditions 2 and 3 have 75 and 300 water molecules, respectively, to investigate the effect of hydration on the structure of the HB-PEI membrane; and conditions 4–6 have 75 CO$_2$ molecules with various hydration conditions to investigate the effect of hydration on the amine–CO$_2$ interaction. Seventy-five and 300 water molecules correspond to concentrations of $\sim$0.04 g/cm$^3$, and $\sim$0.13 g/cm$^3$, respectively, while 75 CO$_2$ molecules correspond to $\sim$0.08 g/cm$^3$.

4.2. Equilibration of the HB-PEI Membrane. To perform MD simulations, we used the DREIDING force field combined with the F3C (water) force field to describe interactions between atoms. DREIDING has been reported in literature to effectively describe the interactions of CO$_2$ molecules (including in systems with amine or nitrogen), wherein results have been validated against published or experimental data. The DREIDING force field has the following form:

$$E_{\text{total}} = E_{\text{vdW}} + E_{\text{Q}} + E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} + E_{\text{inversion}}$$

(3)

where $E_{\text{total}}$, $E_{\text{vdW}}$, $E_{\text{Q}}$, $E_{\text{bond}}$, $E_{\text{angle}}$, $E_{\text{torsion}}$, and $E_{\text{inversion}}$ are the total, van der Waals, electrostatic, bond stretching, angle bending, torsion, and inversion energies, respectively. $E_{\text{Q}}$ is
calculated from atomic charges that are obtained from Mulliken population analysis. All MD simulations were performed in LAMMPS.\(^3\) To reach equilibrium states within a reasonable amount of time, we utilized a general annealing procedure outlined by Jang and Goddard that puts the system repeatedly through cycles of thermal and pressure annealing.\(^3\) These repetitive procedures accelerate the equilibration process by proving additional kinetic energy and space to attain the equilibrated structure. It is important to note that no particular geometry was predetermined during the annealing procedure. Subsequently, a 200 ps NVT MD simulation and a 1 ns NPT MD simulation were conducted using Nose–Hoover thermostat to complete the annealing procedure.\(^3\) Finally, the system was submitted to an isothermal–isobaric (NPT) ensemble for 20–30 ns under target conditions (303.15 K and 1 atm) until the potential energy and density were observed to be stable for at least 10 ns (indicating equilibrium). The final 10 ns of this simulation was then used for analysis.

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**Notes**

The authors declare no competing financial interest.

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