Poly(styrene-co-vinylbenzyl chloride-co-divinylbenzene)

PORE SIZE TUNING OF POLY(STYRENE-CO-VINYLBENZYL CHLORIDE-CO-DIVINYLBENZENE) HYPERCROSSLINKED POLYMERS: INSIGHTS FROM MOLECULAR SIMULATIONS

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ABSTRACT

In this study, we present an atomistic simulation study of several structure-property relationships of hypercrosslinked polymers (HCPs) synthesized using styrene (STR), vinylbenzyl chloride (VBC), and divinylbenzene (DVB). Molecular simulation samples were prepared using a virtual polymerization algorithm, *Polymatic*, with DVB contents ranging from 0 to 50 mol%. The HCP polymerization algorithm and the models were validated by comparison with experimental data: BET surface area, pore volume, H₂ and CO₂ loading in 2% DVB samples. Furthermore, the simulated trends in BET surface area and pore volume were in good agreement with the experimental data; both surface areas and pore volumes increased with increased VBC-DVB crosslinking. The same virtual polymerization approach was utilized to study the effect of DVB on the structure and thermodynamic properties of HCPs. Our results demonstrate that DVB mol% significantly altered the structural and gas (H₂, and CO₂) adsorption properties of the sample. Finally, though our data demonstrated that structural properties can be tuned at the atomistic level by varying the DVB mol%, they did not exhibit a significant improvement in the performance of H₂/CO₂ gas separation applications.

KEYWORDS

hypercrosslinked polymer; microporous materials; atomistic simulation

INTRODUCTION

The emergence of microporous materials is introducing novel solutions to current energy and environmental concerns. Microporous materials can possess high surface areas and pore volumes, which give them exceptionally high gas storage capacity capacities [1]. From these characteristics, microporous materials could become a cornerstone for renewable and clean energy, including the utilization of methane or hydrogen. Usually, storing these light gases requires high pressure tanks or cryogenic systems that represent a safety concern or may not be practical. However, by using microporous materials, low pressure gas storage that provides safer and more convenient storage and transportation alternatives could be realized. Moreover, some of these porous materials also have an exceptionally high CO₂ storage capacity, which could ameliorate environmental concerns regarding carbon emissions [2]. Certainly, some of these materials have preferential adsorption of specific gases, which could also improve gas separation processes. For example, hypercrosslinked polymer (HCP) [3], covalent organic polymer (COP) [4], porous polymer network (PPN) [5], and metal-organic framework (MOF) [6] have each been shown to exhibit a relatively high gas selectivity. To date, the most promising porous materials for gas separation and storage are, for example, metal-organic frameworks (MOFs) [7], zeolites [8], covalent-organic frameworks (COFs) [9], and porous organic polymers [10,11].

Hypercrosslinked polymers have several advantages over other porous materials. Slater and Cooper [12] provided a comprehensive comparison of various microporous materials and identified that porous organic polymers (*e.g.* HCPs) generally have a good to excellent stability; and generally more stable than other materials (*e.g.* zeolites, MOFs, covalent organic frameworks, and porous molecular solids). Moreover, several other groups have also pointed that HCPs are robust against physical and thermal stress, moisture, and acidic gases [13–15]. These

intrinsic characteristics are ideal for industrial uses, such as gas separation and storage, when harsh conditions are prevalent. In general, hypercrosslinked polystyrenes have been widely studied and have been used in chromatography [16], filtration [17], and organic vapor capture [18]. In particular, styrene (STR), vinylbenzyl chloride (VBC), and divinylbenzene (DVB) systems have shown promise for gas storage applications that might need high surface areas ($> 2,000 \text{ m}^2/\text{g}$) [19–21]. A systematic study that provides a clear understanding of the key properties that can exploit the tunability of these type of systems is crucial. Molecular simulations can be used to understand and optimize these systems. For example, by studying the effect of the DVB content in these materials, their properties and gas separation performances can be optimized [22]. Additionally, molecular simulations offer an attractive method for rapidly and economically evaluating large numbers of materials. Thus, the most efficient methods for characterizing hypercrosslinked polymers (or any microporous material in general) should include these techniques.

In general, the construction of amorphous materials (*e.g.*, amorphous polymer, hypercrosslinked polymers) in silico is challenging due to the lack of a reference structure (*i.e.*, x-ray crystallography) and the nature of unfavorable energy resulting from steric effects as a function of chain length [23,24]. Several approaches have been attempted to generate the amorphous network structures, such as assuming ordered structures [25–27] or combination of smaller network fragments [28–34]. Unfortunately, these approaches are not ideal for highly crosslinked amorphous systems. Currently, the state-of-the-art approach for constructing amorphous polymeric structures is the use of a ‘simulated polymerization technique’. In simulated polymerizations, approaches involve energy minimizations and molecular dynamics (MD) simulations as new bonds form throughout the synthesis process. By incorporating MD

during polymerization and crosslinking, the system is allowed to equilibrate into a more favorable energy state and a more realistic structure is usually obtained. Simulated polymerizations and crosslinking approaches have been successfully applied to several crosslinked polymer networks in which the mechanical properties (*e.g.*, Bulk modulus, Young's modulus, Shear modulus, and Poisson's ratio) and thermodynamics properties (*e.g.*, density, glass transition temperature, and thermal expansion coefficient) were found to be in good agreement with experimental data [35–38]. Moreover, this approach has also been performed using coarse-grained methods in order to generate a much larger sample size for characterization of macroscopic properties for a longer time scale [39,40].

Recently, we have developed an open-source code, *Polymatic*, that is capable of constructing amorphous polymeric materials that are structurally consistent with experimental samples [24]. *Polymatic* has been used for crosslinked polymeric samples in previous works to reveal many important structure-property relationships. For instance, poly(chloroxylene) was investigated initially, and it was found that the degree of crosslinking significantly affected the microporosity of the system [41]. The simulated H₂ and CH₄ uptake for poly(chloroxylene) using grand canonical Monte Carlo (GCMC) simulations were also consistent with the experimental results. In another study, a copolymer of thermally crosslinked octane-styrene-divinylbenzene (OS-DVB) was investigated, and the relationships between the degree of crosslinking, free volume, glass transition temperatures, and peak shifts in the structure factors were revealed [42]. Recently, the effect of T_g enhancing comonomers was studied, and the simulated results provided consistent composition and surface area relationships that were similar to the experimental results [43]. Poly(styrene-co-vinylbenzyl chloride), has also been studied, and the pore evolution throughout the crosslinking process as well as the changes in pore size

distribution in the swollen and dried states were established [44]. This last study provided a key fundamental understanding of these type of systems. However, several important aspects remain to be investigated. For example, in experimental samples, a small percentage of divinylbenzene (DVB) is usually present in this type of hypercrosslinked polystyrenes in order to create a lightly crosslinked precursors; the presence of DVB was not included in our previous simulations. Incorporating a systematic study of the DVB content into the simulations will allow for a direct comparison of the simulated results with a broader range of available experimental data. Interestingly, one experimental study showed that variations in the DVB content could provide pore size tunability of the hypercrosslinked polymers, which could be crucial for separation processes [45]. If this is the case, the possible benefit from controlling pore size by using DVB should be exploited; in order to achieve this goal, a detail understanding of these systems is needed. Furthermore, the presence of DVB may significantly alter the structure of hypercrosslinked polymers, which could significantly affect the properties of the material. Therefore, in this work, molecular simulations were used to optimize the DVB content in order to maximize the properties and gas separation performance of hypercrosslinked polymers. Initially, the properties of simulated structures were compared to available experimental data to confirm the veracity of our predicted simulations. Then, systematic analyses of varying DVB content on the system were performed in order to account for the effects on the structural and gas adsorption properties. Overall, the results shown below confirmed the accuracy and reliability of simulating amorphous hypercrosslinked polymers and also helped to elucidate the effect of DVB on HCP structures.

METHODS

Simulation methods

In order to mimic the synthesis processes of hypercrosslinked polymers, simulations were performed in two stages, linear polymerization and crosslinking, according to a previous work [44]. In the first stage, the simulation produces a linear polymer chain by linking a vinyl group to each monomer. It is important to mention, however, that any DVB present in the system will serve as a crosslinking molecule, and a pre-crosslinked polymer network will be obtained in this stage. The second stage is implemented to mimic a high degree of crosslinking by VBC, which also serves as a crosslinker. The *Polymatic* code [24,46] was used to control the virtual synthesis process of both steps. The *Polymatic* code performs bond searching and bond formation, and handles communication with Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [19] for energy minimization and both canonical (NVT) and isobaric-isothermal (NPT) molecular dynamics simulations. Two force fields were used for the polymer. Non-bonded interactions were calculated by applying the Transferable Potentials for Phase Equilibria United Atom (TraPPE-UA) potential [48,49], while bonded interactions were evaluated with the Polymer Consistent Force Field (PCFF) [50]. We found that the use of TraPPE-UA/PCFF significantly reduced computational costs and yielded similar structural properties when using PCFF alone. Styrene (STR), vinylbenzyl chloride (VBC), and divinyl benzene (DVB) monomers were built using Materials Studio 7.0 (BIOVIA, CA) and PCFF atom types were assigned (Figure 1A). The atom type nomenclature in Figure 1A (Lc1, Lc2, Ccp, and Cc2) were chosen to identify linker atoms for *Polymatic*. The files were converted using the perl scripts available from the *Polymatic* package. *Polymatic* was used to make new bonds when linker atoms were found within a cutoff distance of 6 Å. During linear polymerization, an Lc1 atom of one monomer was connected to an Lc2 atom of a different monomer, and during crosslinking, a Cc2 atom of one monomer was connected to a Ccp atom of another monomer. Because both VBC

and DVB serve as crosslinking molecules, the crosslinking percentage is defined as the percentage of VBC and DVB molecules in the system. All results presented in this work were based on 4 independent samples. Note that the number of independent samples (*i.e.* independent initial configurations of randomly placed monomers) was reduced from a previous study (from 5 to 4 samples) because the number of monomers was significantly increased (from 200 to 2,000 monomers). Nonetheless, the standard deviations were significantly reduced. For example, HCP with 100% crosslinks, 0% DVB, the error was reduced from $\pm 146 \text{ m}^2/\text{g}$ to $\pm 42 \text{ m}^2/\text{g}$ when the monomers were increased from 200 to 2,000. The composition of monomers for each simulation is summarized in the supplemental information, Table S1.

Figure 1 - (A) Atom types used in styrene (STR), vinylbenzyl chloride (VBC), and divinylbenzene (DVB) monomers. Chlorine atoms were not included in the simulations. (B) The synthesis workflow of hypercrosslinked polymers in silico involving random packing, polymerization, swelling, crosslinking, and structural relaxation using a compression/decompression scheme.

In the algorithm used, the generation of a hypercrosslinked polymer structure involves several steps: (1) random packing of 2,000 monomers at an arbitrarily low density (~ 0.275 g/cm³); (2) polymerization; (3) rescaling to the known bulk density; (4) performing VBC crosslinking; and (5) structural relaxation using a compression/decompression scheme [51] (Figure 1B). During polymerization, a time step of 1 fs was used in all Molecular Dynamics (MD) simulations. All of the MD simulations employed the Nosé-Hoover thermostat and barostat with the standard velocity-Verlet integrator. A cutoff distance of 15 Å was used for the Lennard-Jones interactions and the Ewald summation method was used to account for long-range Coulombic interactions. Energy minimizations were performed before every NVT and NPT simulation using the so-called ‘quickmin’ damped dynamics followed by the implementation of a conjugate gradient with the quadratic line search algorithm. The minimization algorithm, quickmin, is available in LAMMPS and it is a damped dynamic routine that projects the velocity along the force vector for each atom to make the minimization more efficient [52,53]. NVT simulations were performed every 5 bond formations for 10 ps, and NPT simulations were performed every 3 NVT cycles for 10 ps. In other words, this means that after five bonds are formed, a short NVT or NPT MD simulation is performed. An NPT MD is performed every two NVT, e.g. 5th bond = NVT, 10th bond = NVT, 15th bond = NPT, 20th bond = NVT, 25th bond = NVT, 30th bond = NPT, etc. The temperature was set to 600 K for NVT simulations and to 400 K at 1 atm for NPT simulations. If no linker atoms were found within the pre-determined cutoff, Polymatic initiated an NVT simulation for 4 ps, followed by a new search until the maximum

number of 500 attempts was reached. The final density after polymerization was about ~ 0.8 g/cm³.

Prior to crosslinking, the system was ‘swollen’ by rescaling its density, which mimicked the experimental procedure in which the polymer was suspended in dichloroethane. In our previous study [44], several swollen densities (0.6 to 0.9 g/cm³) were tested, and it was found that a density of 0.6 g/cm³ produced the result that was most consistent with the experimental data. Therefore, this density was used in this study. After rescaling the box size, an energy minimization was performed (following a similar procedure as that described above) and subsequently followed by an NVT simulation at 300 K, which was performed for 100 ps to equilibrate the system prior to crosslinking. During crosslinking, NVT simulations at 300 K were performed for 10 ps for every 5 bonds formed. If no linking atoms were found within the cutoff, a 5 ps NVT simulation at 300 K was initiated and the bond search was attempted again until a specified maximum number of attempts was reached. Similarly to a previous work [44], a shifted Lennard-Jones cutoff (5 Å) was used in order to mimic the swollen state of the polymer during crosslinking. After crosslinking using VBC, the potential was shifted back to a cutoff of 15 Å and the sample was subjected to a compression/decompression scheme [51] ($T_{\text{max}} = 800$ K, $T_{\text{final}} = 300$ K, $P_{\text{max}} = 50,000$ atm, $P_{\text{final}} = 1$ atm) to relax the structure for further characterization.

Structural characterization

PoreBlazer [54] was used to determine geometric surface area, helium pore volume, void volume, and pore size distributions. The bulk densities of the final structures obtained after applying the compression/decompression scheme are also reported. The geometric surface areas were calculated using the summation of non-overlapping surface areas between the polymer matrix and a nitrogen probe (3.681 Å). Helium pore volumes were calculated from the

adsorption second virial coefficient [55] using the Widom insertion method with a He probe at 300 K and 10^6 insertion trials. In this work, the helium pore volume was taken as equivalent to the micropore volume because the generated samples only contained pores of less than 2 nm (*i.e.*, the sample did not contain mesopores or macropores). The pore size distributions were calculated by differentiation of the geometric pore volume as a function of probe size ($PSD = -dV(d)/dd$). The geometric pore volume, $V(d)$, was determined by Monte Carlo insertions and the summation of incremental probes. The calculation was based on 500 tests of 10^6 insertions/test with a 0.02 Å bin size. The geometric pore volume, $V(d)$, from each sample was smoothened using a MATLAB function with a 51 data point span (± 0.5 Å) averaged over at least 4 independent samples prior to differentiation.

Radial distribution function and structure factor

Radial distribution functions (RDF) were calculated using LAMMPS from NPT simulations at 300 K and 1 atm for 10 ps. Note that because pairwise interactions between 1-2 and 1-3 bonded atoms were not employed, these atoms were not in the neighbor list; therefore, their $g(r)$ values were not calculated (no peak less than ~ 2.5 Å). The structure factors, $S(q)$, were determined using the Interactive Structure Analysis of Amorphous and Crystalline Systems (I.S.A.A.C.S) [56] with 10,000 steps.

Gas adsorption and selectivity

The adsorptions of H_2 and CO_2 gasses on the hypercrosslinked polymers studied in this work were calculated using the MCCCS-MN (Monte Carlo for Complex Chemical Systems-Minnesota) software [57]. The Lennard-Jones parameters for H_2 and CO_2 were obtained from a previous work by Darkrim and Levesque [58] and from the TraPPE-UA potential [59], respectively. The simulations were performed using the isobaric-isothermal (*NPT*) version of the

Gibbs Ensemble Monte Carlo (NPT-GEMC) simulations, which included the probabilities of translational, rotational, volume changes and particle swaps between two simulation boxes [60,61]. During all adsorption simulations, the polymer model was held rigid. For all simulations, the maximum displacements and volume moves were adjusted during the equilibration to yield acceptance rates of close to 50% and 40%, respectively. The simulations included equilibration and production periods with at least 2×10^7 and 4×10^7 MC steps, respectively.

In order to evaluate the gas-separation (H_2/CO_2) performance of the HCP materials with varying DVB mol%, the adsorption evaluation criteria for pressure swing adsorption (PSA) applications were investigated as proposed by Bae and Snurr [62]. The five criteria were CO_2 uptake (N_i^{ads}), CO_2 working capacity (ΔN_i), regenerability (R), selectivity during adsorption (α_{ij}^{ads}), and sorbent selection parameter (S). The equations for these criteria are shown explicitly below (where i and j are CO_2 and H_2 , respectively, and y is the molar ratio of gas in the bulk phase):

$$\Delta N_i = N_i^{ads} - N_i^{des} \quad (\text{Eq. 1})$$

$$R = (\Delta N_i / N_i^{ads}) \times 100 \quad (\text{Eq. 2})$$

$$\alpha_{ij}^{ads} = \left(\frac{N_i^{ads}}{N_j^{ads}} \right) \left(\frac{y_j}{y_i} \right) \quad (\text{Eq. 3})$$

$$S = (\alpha_{ij}^{ads})^2 / (\alpha_{ij}^{des}) (\Delta N_i / \Delta N_j) \quad (\text{Eq. 4})$$

RESULTS

Sample validation

In this section, the experimental data available in the literature for the STR-VBC-DVB hypercrosslinked polymers at 2% DVB were compared with the results of our simulated samples (Figure 2). This step was essential in validating the structure generation algorithm and the

molecular models implemented in this study. This validation, in return, provided confidence in using the atomistic molecular simulations performed in this work to predict the performance of STR-VBC-DVB materials. Specifically, the surface area, micropore volume, and gas adsorption were used for comparison because these are important parameters for gas capture, storage, and adsorption-based separation processes.

Figure 2 - Validation of simulated samples with experimental data. The samples were based on 2% DVB hypercrosslinked polymer. (A) Surface area comparison at different crosslinks percentage. (B) Micropore volume comparison at different crosslinks percentage. The micropore volumes from experiments were obtained from nitrogen adsorption isotherms at $P/P_o = 0.14$ [43]. (C) The comparison of excess hydrogen adsorption at 77 K for 2% DVB, 100% crosslinked sample, with an experimental estimated pore size of 1.8 nm (100% VBC-DVB) [63] (D) Comparison of CO_2 storage capacity for 2% DVB, 100% crosslinked sample at 300 K. The simulated sample (black square) and experimental data [15,21,43,45,64] (white square) were

based on the same system, 2% DVB, 100% crosslinked (100% VBC-DVB). Experimental results for metal-organic frameworks (MOFs) and microporous organic polymers (MOPs) were reproduced from review papers by Sumida *et al.* [65] and Dawson *et al.* [66] and the data were provided herein to show the performance of HCP relative to other class of materials.

In molecular simulations, the geometric surface areas (SA_{GEO}) can be obtained easily, and thus the use of SA_{GEO} is a preferred method for simulated samples. In some instances, SA_{GEO} may be directly compared with the experimental BET surface areas (SA_{BET}) [67]. Note that the BET surface areas can also be obtained by molecular simulation using Grand Canonical Monte Carlo (GCMC) or Gibbs Ensemble Monte Carlo (GEMC); however, these methods are expensive because simulations of nitrogen loading at different pressures must be performed in order to determine the surface areas from the BET equation. Comparisons across both methods must be employed with caution because the approaches used in surface area determination are fundamentally different. In simulations, the SA_{GEO} is determined by the summation of the non-overlapping SA_{GEO} of the polymer atoms and a nitrogen probe [54]. In experiments and simulations, the SA_{BET} is extracted from the nitrogen adsorption isotherm at 77K and calculated from the BET equation. Moreover, SA_{BET} are based on the accessibility of nitrogen molecules to be physisorbed onto materials in which additional mechanisms, such as capillary condensation and pore filling, may also be present [68]. In our previous study, 115 amorphous microporous materials were tested, and it was found that the comparison between the geometric and BET surface areas is only valid when the geometric surface area is greater than 1,000 m²/g. When a SA_{GEO} area is less than 1,000 m²/g, a good correlation with SA_{BET} is not found, and SA_{GEO} must be corrected before a comparison with SA_{BET} can be made. Thus, in this work, the SA_{GEO} were corrected using the correlation proposed by Abbott *et al.* (unpublished results) in order to properly compare our results with the SA_{BET} (shown below).

$$SA_{BET} \approx SA_{GEO} + 241e^{\frac{-(SA_{GEO}-374)^2}{2 \times 416^2}} \quad (\text{Eq. 5})$$

Overall, the results shown in Figure 2A indicate that the surface areas obtained in this work are consistent with the SA_{BET} reported from experimental studies [43]. Note that a crossover is observed around 75% crosslinks in Figure 2A. However, reliable conclusions on this observation cannot be made due to the lack of errors presented in the experimental data and significantly large deviations observed in other HCP studies. For example, at 100% crosslinks, the reported surface area could vary from 1,466 to 2,090 m^2/g [15,21,43,45,64]; therefore, a crossover may (or may not) be observed depending the experimental data used.

The micropore volume is another important characteristic of microporous materials and is defined as the volume obtained from pores of less than 2 nm in size [69]. The micropore region is a crucial location in which gas storage is maximized by surface adsorption and the pores are small enough for gas selection to occur at the molecular level. Similar to surface area, the comparison between micropore volume reported from simulations or experiments must be used with caution because they are usually obtained by different methods. As described in the methodology section, the micropore volume for the simulated structures presented herein was obtained by using the helium insertion method at 300 K [55], which provides a representation of a helium porosimetry measurement. By contrast in the experiments, the micropore volume is usually obtained by helium porosimetry or from nitrogen isotherms [43]. As shown in Figure 2B, the micropore volume obtained from the simulations on this work were in good agreement with the available experimental data. As explained previously, the lack of statistical uncertainty in experimental data hindered any interpretation of the crossover around 75% crosslinks. The largest deviation was observed at 60% crosslinking, but the cause of this difference is unclear at this time.

Excess adsorption is the amount of gas that adsorbs only onto the surface of a porous material and can be determined by subtracting the amount of bulk gas in the pores from the total adsorption ($n_{\text{ex}} = n_{\text{tot}} - \rho V$). At low pressures, the amount of bulk gas in the pores (ρV) is negligible and therefore $n_{\text{ex}} \approx n_{\text{tot}}$; however, bulk gas contribution can be large at high pressures due to the compression of gas within the pores. Additionally, it has been shown that HCPs with a variety of crosslinking degrees can contain approximately 60% micropores [43] (< 2 nm). Moreover, the experimental pore size distribution showed that mesopores (2 to 50 nm) and macropores (> 50 nm) may be present within the materials, especially when the DVB content is low [21,45]. When the DVB content is higher, only micropores have been observed. Thus, in this work, we have elected to study in detail only the gas adsorption within the micropore region as a good representation of the numerous HCP systems that are within the limits of current atomistic simulations. Therefore, only surface adsorption was used for a fair comparison, *i.e.*, we used excess adsorption in order to compare the results with the experimental data, especially at high pressures. Specifically, hydrogen adsorption at 77 K is presented in Figure 2C, and the results show that a good agreement was obtained between the experimental and predicted data. **Note that this HCPs had a reported mean pore size of 1.8 nm, estimated by the Tarazona DFT method, and from their work it can be seen that the majority of smaller pores (< 3 nm) contributed to the observed surface area [63,64]. The estimated pore size distribution from DFT, however, does not provide a clear resolution from 0 to 2 nm.** The largest deviation consistently occurred in the lower pressure region, where the simulation over predicted H_2 adsorption by about ~ 0.5 wt%. The discrepancy of gas adsorption in this region has been observed previously in polymers of intrinsic microporosity (PIM) [70]. This phenomenon may be due to the slow structural equilibration of the polymeric matrix [68]. Carbon dioxide adsorption at low pressure is shown

in Figure 2D. Unfortunately, only one data point was available for a similar system. Most importantly, our results confirmed that this hypercrosslinked polymer is a promising candidate for CO₂ storage at high pressure; the capacity of this polymer is comparable to other classes of materials, such as metal-organic frameworks (MOFs) and microporous organic polymers (MOPs). Note that our simulations were performed at pressures of up to 20 bars. These results can be viewed as a conservative baseline. Under very high pressure conditions, gas storage capacity will be even higher if mesopores and/or macropores are present due to the bulk gas contribution (pV).

Effect of DVB on the structure of hypercrosslinked polymer

Prior to using DVB as a pore tuning agent, the impact of this molecule on the structure of microporous polymers should be addressed. The presence of DVB could affect several important parameters, such as density, surface area, pore volume, and gas adsorption capacity; therefore, an investigation of how DVB influences these variables is crucially relevant. Our results show that DVB significantly affected the structure of the microporous polymer. When crosslinking was greater than 60%, the DVB content dramatically increased the density (Figure 3A) and decreased the surface area and pore volume (Figure 3B and 3C). The restriction of pore size by DVB also significantly limited the total H₂ loading capacity (Figure 3D). Because VBC and DVB are crosslinking bridges with different molecular lengths (Figure 4), the shorter DVB bridge will make the material denser, thereby reducing the surface area and pore volume. In general, our data are consistent with experimental studies showing that high DVB contents resulted in a significant decrease in the surface area, which occurred concomitantly with a reduction in H₂ adsorption [21,45]. Only one study by Li *et al.* [45] showed that the surface area, pore volume, and H₂ gas adsorption were highest when the DVB content was low ($0 < \text{DVB\%} < 5\%$). At DVB

contents of greater than 5%, a continuous decline in these parameters was observed. According to their data, the maximum surface area, pore volume, and H₂ gas adsorption occurred approximately 0.5% to 5% DVB. This maximum behavior was not observed in the computer simulations performed in this work. A reduction of the mesopore and macropore regions should increase microporosity. Therefore, properties such as surface area, pore volume, and gas adsorption should generally increase which was observed in the experiments. Thus, Li *et al.* [45] also concluded that this behavior was related to DVB-induced reduction of the mesopores and macropores. At a higher DVB content, the DVB molecules may eventually start to reduce the micropore size, which should result in decreases in the surface area, pore volume, and H₂ gas adsorption; these changes were observed in both the experiments and the computer simulation.

Figure 3 - The effect of DVB on density, geometric surface area, micropore volume, and total hydrogen adsorption. (A - C) Bulk density, geometric surface area, and micropore volume results after compression/decompression steps. (D) Total H₂ adsorption at 77 K 100% crosslinked samples (100% VBC-DVB) at various DVB content.

Figure 4 - Possible bridge types that can be formed between styrene (STR), vinylbenzyl chloride (VBC), and divinylbenzene (DVB) monomers. It can be observed that the DVB bridge is significantly shorter than STR-VBC or VBC-VBC bridges which will affect the structure of the HCP. In this model, a bond can be made at any sp^2 aromatic carbon and several bonds might be formed in an aromatic ring.

Effect of DVB on pore size distribution

The variation in DVB content has been shown to provide tunability of pore size in a hypercrosslinked polymeric system [45]. The possibility of engineering pore sizes in amorphous materials may be beneficial in tailoring them to specific applications, such as gas separation, chromatography, or other filtration/separation techniques. The effect of DVB on the pore size distribution (PSD) was systematically investigated in this work, and the results are reported in Figure 5. Overall, an increase in crosslinking produced a wider pore size distribution (up to 15 Å). In contrast to the crosslinking effect described above, an increase in DVB content prevented the formation of a broader pore size distribution; this behavior was clearly observed in the 75% and 100% crosslinked systems. From our simulations, this effect in the micropore region was caused by DVB and showed a trend that was similar to the experimental results of Ahn *et al.* [21] and Li *et al.* [45], in which an increase in DVB content significantly reduced the sizes of the larger pores within the polymer. In other words, DVB served as a shorter bridge within the

412 hypercrosslinked polymer when compared to the VBC bridge (Figure 4); thus, an increase in the
413 DVB content resulted in smaller pore sizes at the same degree crosslinking. More importantly,
414 the molecular simulations provided a detailed pore size distribution in the micropore region,
415 which was ambiguous in the experimental work [71] due to limitations caused by the size of the
416 (gas) probe and the assumption of pore geometry during the PSD construction. Experimentally,
417 pore size distribution can be obtained from adsorption isotherms and non-local density functional
418 theory (NLDFT) kernels. However, this method has been found to produce artificial gaps at 1
419 and 2 nm, especially in disordered microporous carbon materials [72]. Our PSD data suggest that
420 variations in the DVB content and crosslinking percentage can easily tune the pore size
421 distribution in the micropore region, which was not previously observed in detail. The ability to
422 engineer pore size distribution in the micropore region (< 2 nm) could be extremely beneficial in
423 some specific applications.

Figure 5 - The effect of DVB on pore size distribution (PSD) as a function of crosslink percentage.

Radial distribution functions and structure factors

Radial distribution functions (RDF) are important structural characteristics that provide insights with regards to atomic packing. In molecular simulations, RDF can be obtained based on an atom's coordinates. In order to investigate how DVB affects porosity, the packing between a carbon attached to an aromatic ring (*C) was monitored (*i.e.*, -*CHX-CH₂-, where X represents an aromatic ring). In this approach, the radial distribution function represents the atomic packing of 'backbone' atoms (*i.e.*, atoms that are linearly connected during polymerization, excluding the atoms in aromatic rings or crosslinking units).

The effect of DVB on polymer packing was observed by the presence of several peaks on the RDF (Figure 6A). For example, at 0% DVB content, an increase in crosslinking enhanced the intensity of the peak located near 4.9 Å. This peak represents the *C distance that was optimal for atomic packing of the polymer. An increase in the intensity of this peak produced samples with lower densities and greater surface areas, pore volumes, and gas adsorption capacities. Notably, this 4.9 Å distance was not related to the VBC crosslinks because the distance between the *C of a VBC bridge was larger, ranging between ~ 7 to 9 Å (Figure 4A). Therefore, the peak approximately at 7.2 Å was associated with VBC crosslinking. This observation was also supported by a slight increase in the intensity of the peak at 7.2 Å as a function of crosslinking percentage. At 50% DVB content (Figure 6B), it was inferred that the presence of DVB molecules directly affected the sample's structure because the intensity of the peak at 4.9 Å did not dramatically increase as a function of the degree of crosslinking. Thus, it can be concluded that the DVB molecules significantly restricted preferred atomic packing and prevented the formation of pores because the RDF curves remained relatively unchanged as a function of the crosslinking percentage. Moreover, in the 50% DVB sample, an additional peak ~ 7.5 to 8.1 Å was observed (Figure 6B). Because the presence of this peak emerged as the DVB content was increased and it was not a function of the crosslinking percentage, the peak had to be associated with DVB content and may have been a representation of the *C distance between DVB and its second adjacent monomer (which was determined to be ~ 8 Å via inspection using VMD, a molecular visualization software).

Figure 6 - The effects of DVB on radial distribution functions and structure factors. (A), (B) Radial distribution function, $g(r)$, between *C carbon on polymer chain. On the polymer, *C represents carbon atoms that directly connect to an aromatic ring (-*CHX-CH₂-, where X is the aromatic ring). (C), (D) Simulated X-ray scattering data in terms of structure factor, $S(q)$. Radial distribution function and structure factor pattern for other DVB content are reported in the supplementary section (Figure S1 & S2).

The structure factor, $S(q)$, is another important structural characteristic that can be obtained from X-ray scattering experiments. RDF and structure factors are mathematically related, and the detailed derivation can be found elsewhere [73]. Because X-ray scattering data are more pervasive than radial distribution functions, it is beneficial to calculate structure factors from the simulation samples, which can then be compared against the experimental samples when they become available. Our result showed that without DVB, the intensity in the low- q

region (0.2 to $0.6 \text{ \AA}^{-1}$) increased as a function of crosslinking percentage (Figure 6C). In this low-q region, a systematic study of a polymer with intrinsic microporosity (PIM-1) suggested that an increase in intensity in this region is directly related to an increase in the porosity of the material [74]. At 50% DVB content (Figure 6D), our result showed that DVB restricted the formation of porosity, which is consistent with the data presented above. In the same study, McDermott *et al.* [74] found a peak at the high-q region (approximately $1.35 \text{ \AA}^{-1}$) that represented a specific pore size, as suggested by a monodisperse Percus-Yevick hard sphere model and the Guinier equation. For instance, according to this model, a left shift of this peak will denote an increase in pore size. At 0% DVB content, a high-q peak ($q = 1.35 \text{ \AA}^{-1}$) became broader as a function of the crosslinking percentage, which suggested increased variation in the pore sizes. At 50% DVB content, however, this particular peak remained relatively constant, which indicated that pore sizes were not significantly altered as a function of the degree of crosslinking. Both of these observations are consistent with the PSD data presented in Figure 5.

Ring distributions

The ring distributions in the hypercrosslinked polymers varied significantly at various crosslinking percentages and DVB contents. In this work, we defined the number of crosslinks per ring by the number of new bonds formed during the crosslinking step (*i.e.*, the new linkages between Ccp and Cc2 atoms in Figure 1A). Moreover, if a DVB molecule successfully formed a linkage during the polymerization step, one crosslink was accounted for in addition to any new bonds formed at the Ccp sites during crosslinking. The effect of DVB on the ring distribution is demonstrated in Figure 7. An increase in DVB content generally increased the percentage of the ‘0 crosslink per ring’ column and decreased the percentage of ‘2 or greater’ crosslinks per ring. We observed that an increase in the percentage of 0 crosslinks per ring came from both STR and

DVB as a function of DVB content (Black bars in Figure S3 and S5). The trend of 1 crosslink per ring varied greatly depending on the crosslinking percentage and type of monomer. For example, STR generally showed 1 fewer crosslink per ring while VBC showed 1 additional crosslink per ring as a function of DVB content (Figure S3 and S4). DVB had a decrease in 1 crosslink per ring at crosslinking percentages between 25 to 50%, and the number of crosslinks per ring remained relatively constant at crosslinking percentages above 75% (Figure S5). The percentage of 2 or greater crosslinks per ring decreased as a function of DVB content for all monomer types (*i.e.*, STR, VBC, and DVB) (Figure S3 to S5). The results also showed that the percentage of 4 crosslinks per ring was relatively low, and 5 crosslinks per ring was rarely observed. Moreover, the VBC-VBC triple ring crosslink shown in Figure 4 was not found in our samples, in contrast with experimental speculations. From this result, the higher percentage of 2 or greater crosslinks per ring indicated a greater number of samples with lower densities, higher surface areas, and higher pore volumes (Figure S6) because the percentage of 2 or greater crosslinks per ring was correlated with the crosslinking percentage.

Figure 7 - Ring distribution as a function of crosslink percentage and DVB content. The variation in the number of crosslinks per ring within each system is shown.

Selectivity of CO₂/H₂ gas mixtures

The ultimate goal of pore size tuning is to improve selectivity in separation processes. In recent decades, the use of hydrogen as a clean energy source has drawn interest from the federal and scientific communities [75]. The only product of hydrogen fuel during combustion is water, which is extremely desirable for environmental and global sustainability reasons. Hydrogen gas can be produced by established industrial processes, such as steam reforming and water-gas shift processes, which result in a mixture of mostly H₂ and CO₂ [76]. Eventually, the H₂/CO₂ mixture must be separated; hypercrosslinked polymers have been shown to be promising candidates for this application [14].

The gas selectivity of H₂/CO₂ may be improved by the means of tuning the pore size distribution in order to exploit the molecular size differences of the gases. By varying the pore size distribution using DVB, gas selectivity may be altered. Therefore, we were interested in simulating gas selectivity in order to evaluate the performance of the hypercrosslinked polymers at various DVB concentrations (*i.e.*, variation in pore size distribution) as shown in Table 1. Our result showed that these hypercrosslinked polymers are promising for adsorption-based H₂/CO₂ separation. The percent regenerability (R) is an important parameter that is defined as the amount of adsorption sites regenerated between adsorption and desorption cycles. Our results indicated that nearly all of the adsorption sites were regenerated after desorption at these operating pressures. In a pressure swing adsorption process, it is important to account for the amount of gas that can be removed during a given cycle as well as the selectivity. The CO₂ working capacity is defined as the amount of CO₂ that can be removed between cycles; (see Eq. 1). The sorbent selection parameter (S) is used to evaluate the performance of HCP because it accounts for the gas selectivity during adsorption and desorption, and the working capacity of both gases (see Eq. 4). The overall data suggested that hypercrosslinked polymers with low DVB contents are potential candidates for H₂/CO₂ separation in pressure swing adsorption (PSA) processes because of their relatively high CO₂ working capacity and sorbent selection parameter. Our results suggest that simply tuning pore sizes in HCPs is inadequate for improving H₂/CO₂ separation because the sorbent selection parameter was not improved. This observation supports other results that structural properties such as pore size do not always correlate with gas selectivity [62,77]. The comparison of adsorption selectivity (α^{ads}) and CO₂ working capacity with other simulation data in literature is reported in Figure S7.

Table 1 - The performance of HCP in pressure swing adsorption in terms of regenerability (R), CO_2 working capacity (ΔN_1), and sorbent selection parameter (S). In the simulations, the bulk gas phase contained 89% H_2 ($\pm 3\%$) and 11% CO_2 ($\pm 3\%$) which was based on pre-combustion conditions. The operating pressures were $P_{\text{des}} = 100$ kPa and $P_{\text{ads}} = 2,000$ kPa.

100% crosslinked HCP	R (%)	ΔN_1 (mol/kg)	S
0% DVB	94.08	3.54	261 ± 63
2% DVB	94.03	3.53	283 ± 66
20% DVB	91.24	1.85	137 ± 17
50% DVB	90.21	0.91	150 ± 18

CONCLUSIONS

We demonstrated that molecular simulation techniques can be used to describe accurately the surface area, pore volume, and gas loading of hypercrosslinked polymers synthesized using styrene (STR), vinylbenzyl chloride (VBC), and divinyl benzene (DVB). The ability to predict these properties is crucial for performance optimization and materials selection. Molecular simulation were employed to predict how DVB can affect the structural and adsorption properties of these hypercrosslinked polymers. It was found that structural properties can be precisely tuned at the atomistic level by varying the DVB content. However, this tuning does not result in a significant improvement in the performance of H_2/CO_2 gas separation applications. In other words, our result indicated that using DVB to simply tune the pore size in the microporous region in these types of hypercrosslinked polymers is insufficient for improving the H_2/CO_2 gas separation. Nonetheless, our results also showed that VBC-DVB hypercrosslinked polymers are an extremely promising material for CO_2 capture and storage, which is consistent with previous experimental observations.

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