The Influence of Acid Group Clustering on the Thermal and Mechanical Properties of a Self-Healing Polymer

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Abstract

To better understand the molecular level mechanisms behind the self-healing of polymer systems, this work developed and validated a molecular dynamics model for a self-healing polymer, Surlyn® 8940. The polymer chains were built using a free-radical polymerization between ethylene monomers (~95 mol %) and methacrylic acid monomers. Predicted thermal and structural properties including thermal conductivity, heat capacity, transition temperatures, thermal expansion coefficient, density, and Young’s modulus were shown to be in good agreement with experimental values. Furthermore, the effects of cluster formation among the acid groups on these properties were explored.

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INTRODUCTION

System reliability is critical in aerospace applications, in which accomplishing a mission is directly dependent upon retention of structural integrity. Self-healing materials provide a route for increasing damage tolerance and enhancing reliability while also minimizing the time and effort required for repairs. In recent years, many strategies and materials have been developed and studied to enable self-healing in structures and materials. Current self-healing strategies are categorized as either passive or active, and limited or repeatable.

Significant attention has been paid to a passive self-healing strategy in which polymer-filled capsules, hollow fibers, or micro-vascular channels are embedded into host materials in locations where cracks are expected to occur. Upon crack formation and propagation, the capsules rupture and their contents fill in the void to “heal” the host material, preventing catastrophic failure. Because the repair material is depleted during the process, this strategy is not appropriate for conditions where damage occurs repeatedly.

Other self-healing materials are molecularly designed to repeatedly heal, but usually require a stimulus to activate the healing process after the damage event. In some composite materials, heat can be applied to a damaged site to allow for the matrix material to flow and reseal the wound. Similarly, the application of heat can be used to drive reversible Diels-Alder reactions to form chemical cross-links between polymers. Compressive mechanical force is sufficient for repairing damage in some supramolecular materials, such as polymers containing strong hydrogen-bonding end groups, as developed by Leibler and coworkers.

In contrast, the applications which motivate the present work require self-healing materials capable of repeated, autonomous, and rapid damage recovery. The puncture
healing polymers Surlyn® 8940 and Nucrel®, both developed by DuPont, are examples of this class of materials and are capable of sealing ballistic wounds within microseconds of the puncture event. Of the ballistic self-healing polymers in the literature, Surlyn® 8940 exhibits the highest efficacy with respect to healing.

Surlyn® 8940 is a random copolymer mixture of ethylene (94.6 mol%) and methyl acrylic acid (5.4 mol%). After radical polymerization of the monomers at high temperature and pressure, the polymer is treated with highly concentrated NaOH to neutralize 30% of the acid groups. Other Surlyn® 8940 derivatives exist with differing ethylene:methyl acrylic acid ratios and extents of ionization. Nucrel®, for example, has the same molar composition as Surlyn® 8940, but all of its acid groups are protonated.

While some experimental ambiguity about the detailed damage processes occurring in these materials remains, the ballistic penetration event is primarily an elastic deformation. A combination of bulk elastic recovery, polymer re-entanglement, and the reformation of ionic bonds cause the material to return to its original shape after a recovery period. The experimental data suggests that material heating in the zone around the puncture site makes the polymer chains sufficiently mobile to re-entangle, and for the ionic or acidic functional groups to reform into clusters. High-speed video evidence suggests a shock wave precedes the penetrator in reaching the exit side of the sample. In either case, a small fraction of the deformed material is lost, with the majority returning to its initial shape.

Many of the details of the recovery process depend on the physical and chemical properties of the particular material under investigation, the details of the test method, and the environmental conditions under which the test is performed. The most important material characteristics are polymer backbone flexibility and the presence of side
chain functional groups capable of forming clusters. While these cluster forming functional
groups are often ionic, the observation of self-healing behavior in the fully protonated
polymer Nucrel® shows that this is not a requirement.\textsuperscript{8a,8c} Aggregation of cluster forming
groups can be enhanced by blending additives into the material,\textsuperscript{8c} although additive
concentration must be limited to avoid loss of self-healing behavior. While this effect is
not fully understood, it appears that the additive may be acting as both a plasticizer for the
chain backbone and a cluster-promoting agent. This is consistent with the effect of added
oxalic acid, which significantly improves healing behavior while simultaneously reducing
elastic modulus.\textsuperscript{8d}

The key difference among different test methods is the generation of heat at the damage
site. Both sawing-induced damage and ballistic penetration result in local heating and self-
healing, although in the latter case this behavior is relatively insensitive to details like bullet
size and velocity.\textsuperscript{8c} Low velocity punctures and clean cuts by a sharp blade do not
significantly increase local temperature and do not self-heal. Finally, the primary
environmental condition that must be controlled is temperature.

A common characteristic of ballistic self-healing polymers is the existence of an
order/disorder transition temperature ($T_o$), which is found between the glass transition
temperature ($T_g$) and the melting temperature ($T_m$).\textsuperscript{8b} In order for healing to occur, the
ambient temperature must be greater than the glass transition temperature, to enable chain
mobility and re-entanglement, but lower than the order-disorder transition, above which
the acid group clustering is greatly diminished.\textsuperscript{8b} Elastic recovery will still occur above the
order-disorder transition, up to the melting temperature, but the mechanical properties of
the polymer will reduced due to the limited reformation of acid group clusters. Recovery
of acid group clustering after the polymer is heated beyond Tm is a slow process, requiring about 24 hours.\textsuperscript{8b}

This brief overview shows that there is broad understanding of many qualitative details of self-healing, but a more comprehensive quantitative framework is lacking. Rational design of application tailored self-healing materials requires a better understanding of the connection between the molecular-scale structural and chemical details of the material, and its macroscopic properties and behavior. This work describes some initial steps in this direction, including the development of an atomistic model for Surlyn\textsuperscript{®} 8940, and the use of molecular dynamics simulations to predict a number of thermal and mechanical properties relevant to self-healing. The performance of this model has been assessed by validating the simulation results against experimental data. Specifically, the model has been validated by comparing predicted density, Young’s modulus, heat capacity, thermal expansion coefficient, transition temperatures, and thermal conductivity to experimental measurements. This paper lays the groundwork for future efforts to understand the structure-property relationships for this class of material.

**EXPERIMENTAL**

Surlyn\textsuperscript{®} 8940 samples, provided by Dupont, had an average thickness of 0.6386 cm and were used as received. Its monomeric structure and molar composition can be seen in Figure 1. A Netzsch Heat Flow Meter (HFM) 436 Lambda was utilized to measure thermal conductivity of Surlyn\textsuperscript{®} 8940 polymer. A Netzsch thermal mechanical analyzer (TMA) was used to acquire thermal expansion coefficients. A static load of 20 cN was applied
while the polymers were heated at a rate of 20 K/min over a temperature range of 283 K to 353 K. A 10-minute isothermal hold at 283 K was applied at the beginning of each run.

SIMULATION DETAILS

All simulations were performed with the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator). After the polymer system was built using the procedure described in the following section, equilibration simulations of various durations were run with a time step of 1.0 fs using the Nosé-Hoover barostat and thermostat to maintain the pressure and temperature in an NPT ensemble at 298 K and 1.0 bar.

After the equilibration, simulations were run to measure Young's modulus, transition temperatures, heat capacity, thermal expansion coefficient, thermal conductivity, and viscosity. For Young's modulus, the length of the simulation cell was increased in the desired direction at a strain rate of 1% per 1 ns over the course of 5 ns. The results from all three directions were averaged and are reported below.

Heat capacity and thermal expansion coefficient were calculated from enthalpy, temperature, and volume measurements taken from three NPT simulations at 290 K, 300 K, and 310 K at a constant pressure of 1.0 bar via equations (1) and (2):

\[
C_p = \left( \frac{\partial H}{\partial T} \right)_p \approx \left( \frac{H_2 - H_1}{T_2 - T_1} \right)
\]  \tag{1}

\[
\alpha = \left( \frac{\partial \ln V}{\partial T} \right)_p \approx \left( \frac{\ln V_2 - \ln V_1}{T_2 - T_1} \right)
\]  \tag{2}

In equation (1), \( C_p \) represents heat capacity and \( H_x \) is the average enthalpy of the system at temperature \( T_x \). In equation (2), \( \alpha \) represents thermal expansion coefficient and \( V_x \) is the average molar volume at temperature \( T_x \).
The transition temperatures were determined by running the equilibrated system at a series of 21 temperatures between 100 and 450 K with a 1 ns equilibration period and a 1 ns data collection period at each temperature. The system was initially annealed to 100 K, equilibrated, and run at that same temperature. The end configuration served as the initial configuration for the next higher temperature simulation and this cycle was repeated until all 21 simulations were completed. Phase change temperatures were identified by significant changes in slope in the density versus temperature plots.

Thermal conductivity and viscosity were measured using the reverse non-equilibrium molecular dynamics (RNEMD) method developed by Müller-Plathe and coworkers. In these simulations the atoms are divided into a number of slabs, N, and the kinetic energy of the hottest atom in slab N is exchanged with the kinetic energy of the coldest atom in slab N/2 over the course of 5 ns. This induces a smooth thermal gradient where slab N/2 will be the hottest and slab N will be the coldest. The thermal conductivity can subsequently be measured from the slope of this gradient. A comparable procedure is used for the calculation of viscosity, but the x-component of velocities are exchanged instead of atomic kinetic energies. Alternative approaches, such as SLLOD could not be used because of their inability to include long-range Coulombic interactions.

POLYMER CONSTRUCTION

For predominantly (~95 mol%) aliphatic hydrocarbon polymers such as Surlyn® 8940, substantial gains in computational efficiency are realized with minimal loss in fidelity by utilizing a united atom model for the CHx repeat units and the methyl groups of the methacrylic acid monomers. The DREIDING force field, known to be accurate and
efficient in modeling related polymer systems,\textsuperscript{13} was utilized for the bonded and non-bonded interactions for the united atom sites in this work. The carboxylic acid sites, however, require explicit representation of all atoms to reliably model the physical interactions believed to be essential in the behavior of Surlyn\textsuperscript{®} 8940. While mixing of force field parameters is generally undesirable, the lack of reliable charges for the acid groups in the DREIDING force field required the adoption of alternative parameters. In this work, atomic charges and van der Waals (vdW) parameters for these groups were taken from the Charmm General Force Field (CGenFF)\textsuperscript{14} because of its demonstrated success in modeling the dimerization of carboxylic acid groups.\textsuperscript{15}

Polymer chains of Surlyn\textsuperscript{®} 8940, with the same stoichiometry as the experimental samples, were built using a free-radical polymerization technique inspired by the work of Perez \textit{et al}\textsuperscript{16} and Farah \textit{et al}.\textsuperscript{17} To begin, 5000 monomers, in the appropriate molar ratios, were randomly placed on a grid in a cubic cell with 70 Å long sides and equilibrated during a 1.0 ns simulation at 500 K and 1350 bar. Radial distribution functions (RDFs) were measured in the equilibrated simulation cell to determine an appropriate interaction distance between potentially reactive sites. This separation, 5.5 Å, was used as the reaction cutoff distance in subsequent polymerization simulations. Some modifications to the methods described in the literature\textsuperscript{16-17} were found to improve the polymer structures and promote entanglement. First, at points in the polymerization when no monomers were within reaction distance, the repulsive interactions between monomers and polymer chains were softened, the interactions between monomers and reactive sites were strengthened, and the radius of the reaction shell was increased. This accelerated the polymerization by allowing the monomers to move past intervening chains to reach reactive sites more
quickly. In addition, the polymerization process was continued until all monomers had reacted, rather than discarding unreacted monomers after some arbitrary number of steps. Trial simulations revealed an initial population of 66 reactive monomers provided acceptable agreement with experimental values for polydispersity and radii of gyration without exceeding available computational resources.

The initial 66 reactive monomers were chosen at random from the full equilibrated system of 5000 monomers. Once a reactive monomer formed a bond with the closest monomer within the reaction cutoff distance, the new bond was assigned a force constant of 300 kcal/mol and an equilibrium distance of 2.50 Å. This softer bond interaction and longer bond length limits the large forces that would be found with standard carbon-carbon bond parameters at the non-equilibrium geometry found immediately after bond formation. The system was equilibrated for 500 fs at 298 K and 1350 bar with these parameters, after which the force constant and equilibrium distance were switched to the standard values found in the DREIDING force field\textsuperscript{13}, 350 kcal/mol and 1.53 Å, respectively. Upon reversion to the DREIDING bond forces, the system was equilibrated for another 500 fs. This process was repeated until no monomers reacted for 10 cycles, whereupon the vDW interactions were altered as described earlier and a short simulation, typically less than 1000 fs, was run until monomers were within reactive distance of a reactive monomer. The vDW interactions were then reverted to their original values and the algorithm continued.

After the polymer chains were built, the reactive groups were converted to terminal methyl carbons and the system pressure was reduced from 1350 bar to 1.0 bar at a constant rate during a 0.5 ns simulation. This was followed by another 0.5 ns equilibration simulation at 1.0 bar. At this point, 30\% of the carboxylic acid groups were randomly
selected to be ionized, thus converting the polymer system from Nucrel® to Surlyn® 8940. The 81 carboxylic groups were converted to carboxylates by removing the O-H bond, replacing the hydrogen atom with a sodium ion, and modifying the charge distribution. A short run to relax high-energy configurations in the modified system was followed by a 1.0 ns equilibration run. The final cubic unit cell had a side length of 65.5Å. The simulation cells prepared in the manner described above will be referred to as “baseline” throughout this paper.

Several modified systems were also prepared to evaluate the sensitivity of the model to the parameters used during its creation. Among these were a large system with double the number of monomers, a high molecular weight system in which the number of chain initiating reactive monomers was limited to 10, and a uniform chain length system in which all chains were constrained to a uniform length. All of these alternative systems exhibited properties very similar to those of the baseline and in poor agreement with experimental values. Polymers in general, and ionomers in particular, require long simulation times to relax to an equilibrium configuration. It was found that increasing the equilibration time from 1.0 ns to 20 ns was required to establish good clustering of the acid side groups, which was necessary to achieve a valid model to compare with experiments. Table 1 summarizes the differences between the baseline case and the well-equilibrated case.

Finally, cubic simulation cells were found to be incompatible with the RNEMD simulations of viscosity and thermal conductivity. Achieving a smooth, steady-state gradient profile requires the use of a simulation cell that is elongated along one axis. A cell with relative dimensions of LxLx3L (L=46.5Å) was used in this work, and care was taken
to ensure that the cell had the same total volume and density of that used in the cubic unit cell simulations.

RESULTS AND DISCUSSIONS

Structural Properties

Density is a convenient parameter for quickly assessing the quality of the force field used to study a polymeric system. For the systems equilibrated for 20 ns, the average density is 0.865 g/cc. This is within 10% of the experimental value of 0.95 g/cc measured for Surlyn® 8940. In view of the substantial difference in molecular weight between the experimental and simulated materials, this magnitude of error was not unexpected. As seen in Table 1, there is little difference in density between the baseline case and the well-equilibrated system. So, while the predicted densities are in reasonably good agreement with experiment, they cannot be used as a metric for determining when the system has reached equilibrium.

While the density was found to be relatively insensitive to equilibration time, the stress-strain plots shown in Figure 2 reflect a significant change in mechanical behavior between the two systems. Specifically, increasing the equilibration time from 1 ns to 20 ns results in a near doubling of the elastic modulus, from 164 MPa to 325 MPa. The agreement of the well-equilibrated model with experiment is quite good, falling within 7% of the experimental bounds. Because of the short chain lengths and very high strain rates used in these simulations, this agreement with experiment is better than expected. Fortuitous cancellation of error cannot be excluded at this time, and future simulations with much larger systems and slower strain rates will be required to confirm these results.
There is broad consensus in the literature that clustering of the acid groups, in both the protonated and ionized forms, plays a critical role in both the self-healing behavior and mechanical properties of ionomers. To check if this clustering mechanism could help explain the significant difference in the tensile moduli calculated for the baseline and well-equilibrated systems, the radial distribution functions between pairs of carbonyl carbons were collected and are compared in Figure 3. These distributions were calculated by averaging the distribution of carbonyl carbon separations, measured during 1 ns simulations, starting from the baseline and well-equilibrated systems. The sharp, narrow peaks found in the RDF for the well-equilibrated system (solid line) indicate the presence of relatively structured clusters of carbonyl carbons in the 4-6 Å range. The broader, featureless peaks seen in the plot for the baseline system (dashed line) provide evidence that the baseline system has not had sufficient equilibration time to develop well-structured clusters.

To evaluate the thermal stability of the clusters, the well-equilibrated simulation cell was heated to 450 K, which is above the order-disorder transition temperature for the clusters, and then rapidly quenched to 300 K to lock in the disordered structure. The stress-strain curve for this system, shown in blue in Figure 2, is very similar to the curve of the baseline system and their moduli differ by only about 10%. Because the temperature ramp and quench were done too rapidly to permit large changes in polymer backbone configurations, the enhanced modulus must be the product of ionic cluster formation rather than any other structural changes occurring during the longer equilibration.

**Thermal Properties and Phase Behavior**
Correctly modeling the thermal properties of this material is critical because self-healing is directly tied to the polymer’s ability to melt and flow to heal the damage at the impact site. Heat capacity ($C_p$) and thermal expansion coefficient ($\alpha$) are two thermodynamic properties that dictate how a material responds to thermal energy input, such as the heating resulting from compression and friction during a ballistic impact. Predicting these values from simulation also provides another point of validation for the model because experimental data are available for comparison. Using the methods described earlier, $C_p$ is predicted to be 1.546 J/g-K for the baseline system and 1.746 J/g-K for the well-equilibrated system, compared to an experimental value of 1.850 J/g-K. The improved agreement with experiment found for the well-equilibrated system indicates that clustering has an important effect on heat capacity. This can be understood by considering the additional thermal energy input that is required to disrupt the ionic and hydrogen bonding in the clusters, which are absent in the baseline model system.\textsuperscript{8b}

The values of $\alpha$ from the baseline system and the well-equilibrated system are 3.10 x 10^{-4} K^{-1} and 2.59 x 10^{-4} K^{-1}, compared to an experimental value of 2.094 x 10^{-4} K^{-1}. While the value calculated for the well-equilibrated system compares more favorably with experiment than the baseline system, the error is still about 20%. This may indicate that, as in the case of the predicted density, the much larger number of vdW interactions between polymer backbone carbon atoms dominates the volumetric behavior of the system. The resistance to expansion arising from the more strongly interacting cluster atoms is reflected in the lower $\alpha$ for the well-equilibrated system, relative to the baseline system.

It is also important that transition temperatures, which characterize the transition points between glassy, ordered, disordered, and melt states, be accurately predicted in simulations.
of self-healing materials. In Figure 4, calculated density is plotted as a function of simulation temperature, along with best fit lines for subsets of the data. The intersections of these best fit lines are identified as the transition temperatures. The gradual change in slope over the range of temperatures considered is commonly observed in simulations due to the limited system size and rapid heating rate. To avoid biasing the transition temperatures found using this procedure, a number of fits to the data were performed. The number of best fit lines was varied between one and six, as was the number of data points allocated to each best fit line in each trial. The optimal number of segments and allocation of points to each segment were determined by a least-squares fitting procedure, using the combined R² values as the measure of quality of fit. The four segments and data point distribution shown in Figure 4 are the best outcome identified. As mentioned above, the temperatures at which these best fit lines intersect were taken to be the transition temperatures and are labeled on the graph for the well-equilibrated system. The results for both simulated systems are compared with experimental data in Table 1.

The vertical dashed lines in Figure 4 represent the experimental transition temperatures measured using DSC. The lines at 173 K, 323.5 K, and 368 K are associated with the glass transition (T₉), the cluster order-disorder transition (T₀), and the melting point (Tₘ) temperatures, respectively. The figure clearly shows that the simulation results for T₉ (193 K) and Tₘ (426 K) are higher than the experimental values by 20 K and 58 K. T₉ and Tₘ, which are true thermodynamic phase transitions in the real material, are difficult to accurately predict with molecular dynamics simulations because of the system size and heating rate issues. The order-disorder transition temperature, on the other hand, agrees very well with the experimental result because the thermal disruption of the clusters is a
localized phenomenon that probes the structure and energetics of a relatively small group of atoms.

When the fitting procedure was repeated for the density-temperature data found in the baseline simulation, the best fit solution indicated that the data was better represented by three lines, rather than four as were required for the well-equilibrated system. As shown in Table 1, this result indicates that the baseline system exhibits $T_g$ and $T_m$, but not an order/disorder transition. This is consistent with earlier indications that clustering did not occur during the short equilibration time used in the baseline system simulation. The disappearance of the order/disorder transition is also observed experimentally for samples that have been heated past the melting point and retested without allowing time for cluster reformation.\textsuperscript{8b}

**Viscosity and Thermal Conductivity**

The discussion to this point has focused on the static and quasistatic properties of Surlyn\textsuperscript{©} 8940, but dynamic properties are critical in applications such as puncture healing. The rate and extent of thermal energy transfer away from the puncture site has a large effect on the structural state and elastic behavior of the material. Thermal conductivity is calculated by swapping the kinetic energy between pairs of atoms in different slices of the simulation cell to achieve a stable temperature gradient between opposing sides of the cell. Swaps are performed periodically to replicate the effect of applying a constant heat flux. The rate at which swaps are performed determines the rate of simulated heat flux. To examine the sensitivity of calculated properties to this rate, 1000, 2000, and 5000 steps between swaps were tested in this work. Figure 6 demonstrates that smooth gradients were
achieved in each case, although their slopes differ. Using Fourier’s Law, the thermal conductivity is determined by the ratio of total heat flux to the temperature gradient established during the simulation. While the simulations with higher swap rates found higher thermal conductivities, the average over the rates used here was 0.197 W/mK. This result agrees reasonably well with the experimental value of 0.155 W/mK. A very similar thermal conductivity of 0.190 W/mK was calculated for the baseline system, indicating that cluster formation has a small effect on thermal conductivity.

Despite the reasonable results obtained by use of the RNEMD procedure for calculating thermal conductivity, applying it to the calculation of viscosity for this polymer system was unsuccessful. After attempting swap rates of 2, 10, 100, and 1000 with a 1 fs time step, it was found that only the fastest rate, or equivalently the highest shear rate, was able to produce a stable velocity gradient. The viscosity found using this rate was about three orders of magnitude below the experimental value of approximate 13,000 poise. Although this method can be successfully applied for lower molecular weight fluids, the bonding and entanglements found in the present system produces a strong resistance to changes in momentum, making it very difficult to attain a steady-state flux with a reasonable swap rate. Further work will be required to establish a reliable means for predicting the viscosity of this system.

CONCLUSIONS

Understanding the behavior of self-healing materials at the molecular level is essential to the process of tailoring their properties or designing new polymers with the ability to self-heal. The model of Surlyn® 8940 developed in this work is a first step in that direction.
and has been shown to produce reasonably good results with respect to the mechanical and thermal properties. As is usually the case for molecular simulations of macroscopic materials, the results obtained using this model and the simulation procedures described above would be improved by increasing the duration and size of the simulations, at the cost of greater computational expense.

While reproducing the results of experimental measurements is important in model validation, the real value of simulations of this type lies in providing physical insight into the mechanisms that lead to the desirable behavior of the material. The existence of clusters of ionic or hydrogen bonded groups has long been thought to play a role in the self-healing phenomena, but it has been difficult to prove experimentally. As demonstrated in this work, analysis of simulation results can provide a molecular level perspective on this behavior, and support the hypothesis that well-established cluster networks drive many thermal and mechanical properties found in self-healing polymer materials.

In a sense, this system may be viewed as a composite, comprised of nanoscale clusters acting as filler ‘particles’ cross-linked to the matrix polymer. Rather than exhibiting brittle failure, found in more traditional composites, the material maintains toughness due to the dynamic process of ionic and hydrogen bond formation and breakage. While the yield and failure processes were beyond the scope of the present work, they are clearly of interest. Results such as these motivate the future extension of this work to enable computationally guided design of new and more efficient self-healing materials for a range of applications where tolerance of damage and resilience are enabling properties.

REFERENCES


18. DuPont Surlyn® Resins Product Data Sheet.


List of Figure Captions

Figure 1. Composition of monomers in Surlyn® 8940 (a). Snapshot of equilibrated polymer model with clusters of dimers highlighted (b). Backbone carbons are represented by lines, carbonyl carbons are represented by green spheres, oxygens by red spheres, hydrogens by white spheres and sodium ions by yellow spheres.

Figure 2. Stress-strain response of the well-equilibrated system (red diamonds), the baseline system (green triangles), and a de-clustered system (blue circles) along with the upper and lower experimental bounds (thick black lines). Also shown are the best fit lines for each system: well-equilibrated (red solid line), baseline (green dotted line), and de-clustered (blue dashed line).

Figure 3. Radial distribution function between carbonyl carbons from a well-equilibrated system (solid black line) and the baseline system (dashed gray line).

Figure 4. Transition temperature diagram showing the calculated densities (red diamonds) as a function of temperature. The fitted states (solid lines) are shown along with the experimental values (dashed lines) for transitions for clarity.

Figure 5. Temperature profiles at a swap rate of 1000 (red diamonds), 2000 (green triangles), and 5000 (blue circles) steps along with fitted lines.
Figure 1

a) 94.6% \[ \text{C-C} \]_m + 3.78% \[ \text{C-C} \text{CH}_3 \]_n + 1.62% \[ \text{O-O} \text{Na}^+ \]

b) [Image of a molecular structure]
Figure 2.
Figure 3.
Figure 4.
Figure 5.
List of Table Captions

Table 1. Comparison of properties between baseline case, the well-equilibrated case, and the experimental measurements.
Table 1.

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<th>Young's Modulus (MPa)</th>
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<th>Thermal Expansion Coefficient (10^4 \text{ K}^{-1})</th>
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