UNRAVELLING CRITICAL POLYMER PROPERTIES WITH EFFICIENT COMPUTATIONAL APPROACHES

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Caroline M. Krauter, Jacob L. Gavartin, H. Shaun Kwak, Jeffrey M. Sanders, Thomas J.L. Mustard, Alexander Goldberg, Andrea R. Browning, and Mathew D. Halls

Schrödinger GmbH – caroline.krauter@schrodinger.com

Abstract

Establishing relationships between basic chemical composition, structure morphology, and macroscopic materials properties is the key element in the rational design of more robust, better manufacturable and environmentally friendly polymeric products. Recent advances in atomistic modelling and machine learning methods combined with advances in computing technology make these approaches a method of choice for uncovering key structure-property relationship. Especially, recent advances make it possible to use GPU hardware for MD simulations, enabling simulation time scales that were not previously accessible. Long MD trajectories for molecular systems that contain 10^4-10^5 atoms allow to obtain thermodynamic observables with high accuracy. For thermoplastic and rubbery polymers, the ability to model larger systems and longer times, make molecular modeling an increasingly valuable tool for understanding the behavior of industrially relevant polymers. Here, we will use the simulation of the glass transition temperatures (T_g) with molecular dynamics as an example to showcase atomistic-scale simulations for polymer properties.

Introduction

As the use and demands on polymer materials increases, the ability to predict the behavior of the final polymer product gains importance as well. Chemistry and processing parameters are key components in the determination of the final polymer properties. Calculations of properties such as glass transition temperature and modulus based on molecular dynamics (MD) are becoming increasingly popular to speed up the process of assessing chemistry and processing. Recent advances make it possible to use GPU hardware for MD simulations, enabling simulation time scales that were not previously accessible.

An important class of rubber polymers is styrene-butadiene co-polymer rubbers (SBR). During the polymerization reactions of butadiene, *cis*-1,4, *trans*-1,4, or 1,2 (vinyl) monomeric units can be formed (see Figure 1). The content of styrene and vinyl in the SBR co-polymer has a strong effect on the thermophysical properties. More specifically, a higher combined vinyl and styrene content leads to an increase in the glass transition temperature. The chemical composition of the polymer can be influenced through the processing conditions, polymerization mechanism as well as chemical additives and catalysts.
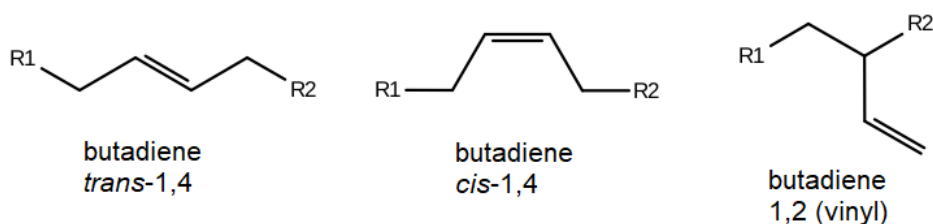
Figure 1: Monomeric units that can be formed during polymerization reaction of butadiene.

In this study we demonstrated the process of constructing a polymer system for molecular dynamics simulation based on the chemical composition and following calculation of the glass transition temperature. In further steps, the effect of, e.g., humidity, molecular additives, or nano-fillers can be included.

Computational Approach

All model building and calculation steps were performed with *the Schrödinger Materials Science Suite 2018-2* [1]. For MD calculations, the GPU-enabled efficient *Desmond* MD engine was used [2,3] in combination with the OPLS3e force field [4,5].

For each co-polymer system, simulation boxes were constructed containing 40 polymer chains with 50 monomer units (assuming random, atactic co-polymer) adding up to approximately 20,000 atoms per box. Table 1 gives the relative composition of the different monomer units. A propagation ratio of 1 was used between all monomer pairs for the construction of the random chain, though this can be easily adjusted to specific ratios depending on the catalyst and additives used in the manufacture. The tangled chain building option of *Schrödinger Materials Science Suite Polymer Builder* and *Disordered System Builder* was used when constructing the simulation boxes. In this build option developed by *Schrödinger*, all the polymer initiators are randomly placed in the simulation cell and are grown in the cell with the backbone dihedral populated according to a Boltzmann distribution at 300 K and targeting an initial density of 0.8 g/cm^3. For each of the co-polymers, three replicates were built and the results were aggregated over all replicas of a type.

The simulation boxes were relaxed using the Compressive Relaxation protocol available in the *Schrödinger Materials Science Suite*. This relaxation protocol allows for efficient relaxation of local structure as well as a high pressure step to remove any excess inner volume and to improve packing. After the relaxation protocol, the systems were equilibrated for an additional 30 ns with an NPT (constant number of atoms, constant pressure, constant temperature) ensemble MD simulation at 300 K and 1 atm with a 2 fs time step to convergence the density at room temperature. Following equilibration at 300K, the simulation boxes were heated to 600 K (the starting point of the thermophysical property calculation) during a 30 ns NPT simulation at 600K.

To calculate T_g, the systems were gradually cooled from a high temperature to a low temperature. The density versus temperature behavior was then used to calculate the T_g. In this study a temperature range of 600 K to 100 K was used with temperature increments of 10 K and NPT equilibration for 10 ns at each temperature. The density versus temperature behavior was evaluated using the *Thermophysical Property Analysis* tool by fitting the data to a hyperbolic curve. The T_g is then calculated as the intersection of the high temperature and low temperature tangents of the hyperbola [6]. The T_g results for the three replicates of each polymer were aggregated using the *Uncertainty Quantification* tool which calculates both the combined T_g and the uncertainty as described in Patrone, et al. [6].

Table 1: Composition and experimental glass transition temperatures of the polymers used in this work. It is assumed that 20% of butadiene is present in the form of *cis*-1,4-butadiene in the random co-polymers.

	Styrene wt%	Vinyl wt%	1,4-butadiene wt%	$T_{g, exp}$ [K]
Buna VSL 2525-0 (Bayer) [7]	25	25	50	225
Sol-5520 [7]	24.7	41.9	35.4	229
SBR Duradene 715 (Firestone) [7]	23.5	46	30.5	238
SBR NS 116 (Nippon Zeon) [7]	23.5	60	20	252
SBR 1500 [7]	23.5	18	58.5	225
Solprene 7201 [8]	40	14.4	45.6	237
SPRINTAN SLR 4601 [9]	21	48	31	248
Poly-*cis*-1,4-butadiene [10]	-	-	100	171
Poly-1,2-butadiene [10]	-	100	-	269
Polystyrene [10]	100	-	-	373
Polyisoprene [10]	-	-	-	203

Results and Discussion

Figure 2 shows an example of a simulation box resulting from growing the polymer units by a tangled chain algorithm as described in the previous section and subsequent equilibration of the density to 300K and 1 atm. For all random co-polymers of Table 1, the room temperature density was in the range of 0.92-0.93 g/cm^3. The simulation boxes built using the tangled chain algorithm served as the starting point for the thermophysical property simulations of the glass transition temperature.
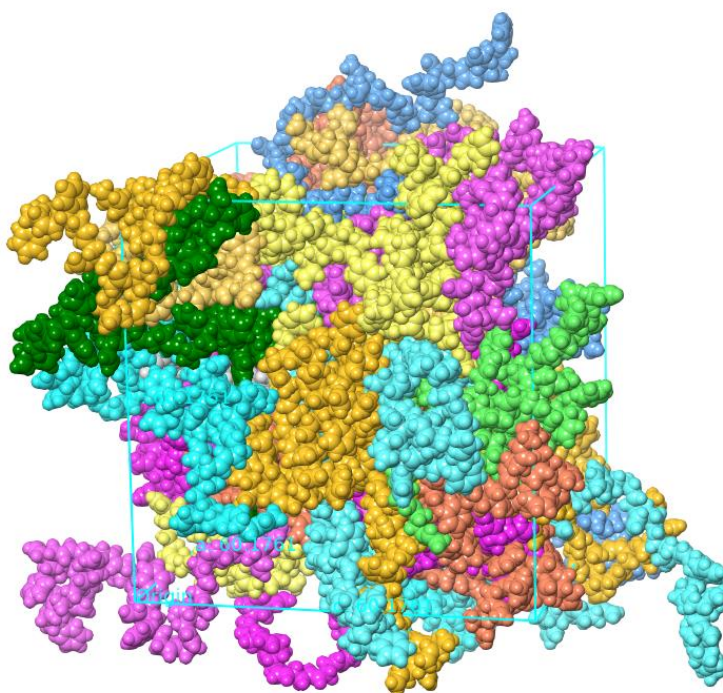

Figure 2: Example simulation box after building with the tangled chain algorithm and equilibration for one of the simulation boxes with the co-polymer Sol-5520. Each polymer chain has a different color to illustrate the entanglement. The box dimension is 60.2 Å × 60.2 Å × 60.2 Å and there are 21,760 atoms in the box (density: 0.93 g/cm^3).

Figure 3 shows the density vs temperature curve for the Sol-5520 system from Figure 2. The glass transition temperature was obtained as described in the Computational Approach section. Due to statistical fluctuations it is important to consider the deviations within each density point and across

multiple simulations. The uncertainty within each simulation was quantified by selecting multiple random subsets of the T_g data. The uncertainty and T_g value for the three replicates was then combined. Figure 4 shows the obtained T_g for the three replicates of Sol-5520 including the corresponding 3σ uncertainty bars. Additionally, the results for the aggregate T_g and uncertainty from the three single calculations is shown including the 3y error ("dark uncertainty" as described in Patrone, et al. [6]) and the 3σ total uncertainty of the aggregate. The analysis of within and replicate simulation uncertainty is essential to detect and avoid noise in the data due to simulation parameters such as too short equilibration times at each temperature step, too small simulation box sizes, or larger-scale structural rearrangements.
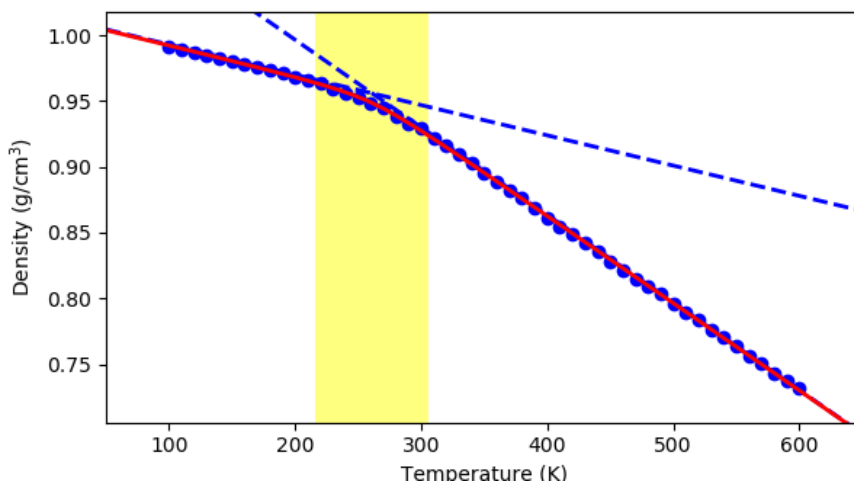

Figure 3: Example of hyperbola fit of density vs. temperature data from thermophysical property calculation to obtain the glass transition temperature (system: Sol-5520 with composition according to Table1).
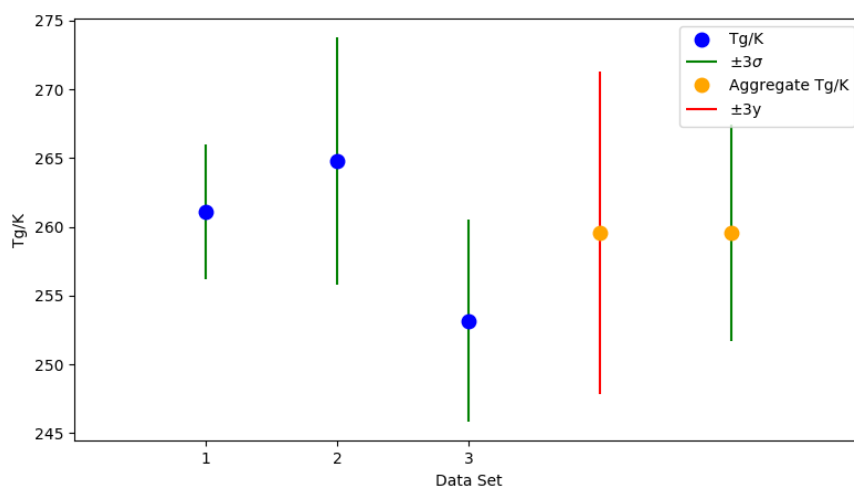

Figure 4: Example of uncertainty evaluation for the three data points (blue) and aggregate data (orange) according to [6].

Figure 5 shows the results for the T_g, aggregated over the independent simulations including the uncertainties for the random SBR co-polymers from Table 1. For comparison, data for the homo-polymers poly-*cis*-1,4-butadiene, poly-1,2-butdaiene, and polystyrene are included. The simulated values are taken from a previous study performed in combination with the OPLS3 force field [4,5] using simulation boxes with 20 chains of 20 monomers.

Typically, the T_g obtained from MD simulation is higher than experiment by 20-30K [11]. The overestimation of T_g is, however, in many cases a constant offset within a certain class of

materials. This effect can also be observed for the current set of polymers. The linear fit to the data points in Figure 5 has a slope of approximately one and an R^2 value of 0.94 while the y-axis offset of the line is approximately 20 K. Such consistent behavior within this class of materials allows for the computational exploration of novel ideas including new monomers and chain microstructures.
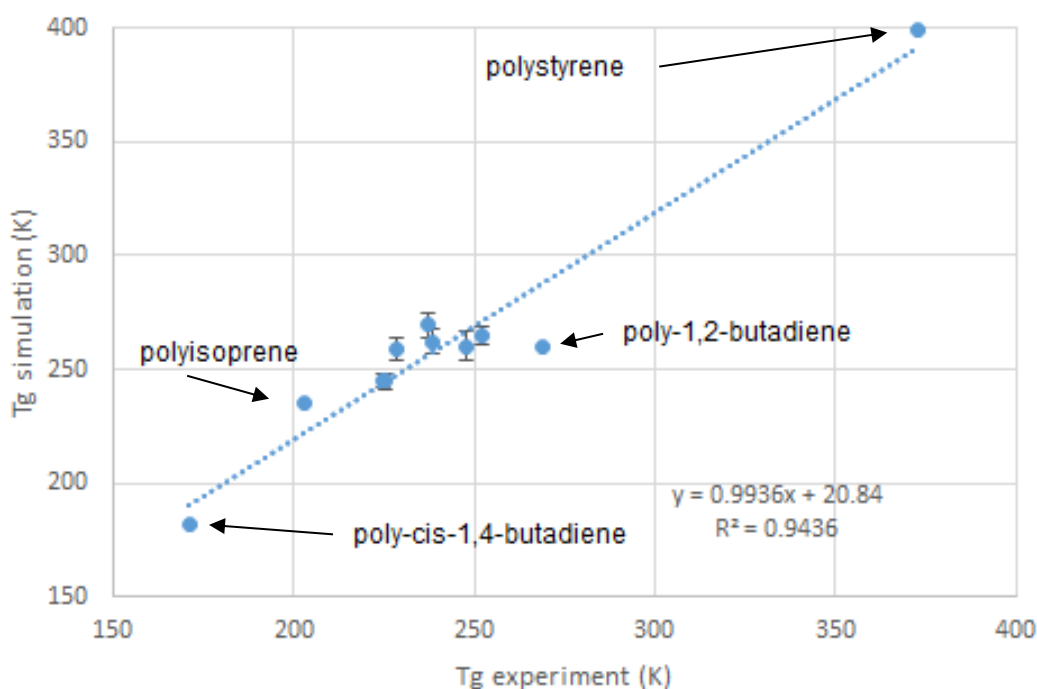

Figure 5: Results for T_g of the different polymers defined in Table 1. The dotted line indicates the linear fit of the data with an R^2-value of 0.94. The error bars indicate one uncertainty deviation for the random co-polymers.

Conclusions and outlook

In the previous section, we have described the construction of polymeric systems for molecular simulation of critical properties like glass transition temperatures. Further important applications of molecular modeling includes the effect of additives, environmental conditions (e.g., chemicals, temperature, humidity) or nanofillers. Through efficient structure builders and advanced computational methods, e.g, grand-canonical Monte-Carlo approaches to load water or other small molecules into the polymer materials until saturation, such effects can be taken into account in many cases. This is schematically illustrated in Figure 6.

By applying coarse-graining techniques to group atoms together into larger particles, system sizes and simulation times can be further expanded. These techniques are particularly helpful in the study of structural aspects of complex formulations. In Figure 6, an example of the aggregation behavior of silica nanofillers within a thermoplastic polymer blend is shown.

Such automated MD workflows in combination with modern quantitative force fields and GPU-acceleration allow for easily accessible, accurate, and efficient prediction of polymer properties. Across this whole range of simulation methods as well as independently, machine learning techniques can be used to extract additional knowledge in regards to how the chemistry and processing impacts the final properties. With the use of simulation to rapidly screen polymer-based materials for multiple properties, the development of new polymer chemistries and formulations to meeting desired characteristics becomes readily achievable.
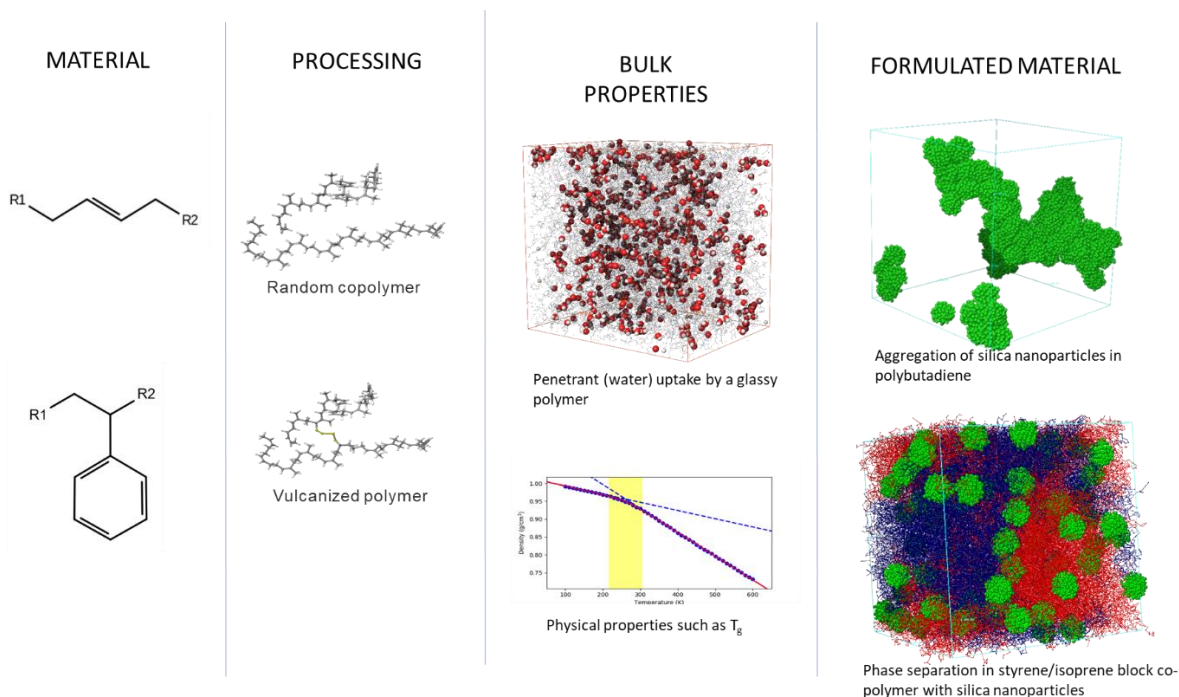
| MATERIAL | PROCESSING | BULK PROPERTIES | FORMULATED MATERIAL |

Random copolymer

Vulcanized polymer

Penetrant (water) uptake by a glassy polymer

Physical properties such as T_g

Aggregation of silica nanoparticles in polybutadiene

Phase separation in styrene/isoprene block co-polymer with silica nanoparticles

Figure 6: Schematic illustration of the different aspects of rubbery materials that can be evaluated with atomistic and coarse-grained simulation methods. The base polymer material (styrene and butadiene used in this example) can be constructed in a manner that mimics the specific processing conditions such as copolymer microstructure and vulcanization across chains. Bulk properties can be simulated to yield base polymer properties. Finally, the structure of formulated materials such as copolymer mixtures and particles in polymers can be simulated with coarse-grained simulations.

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