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**Validating software and force fields for predicting the
mechanical and physical properties of
poly(bisbenzoxazine)s**

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RESEARCH PAPER

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Molecular models for two polymers: (1) based on the monomer 6,6'-*bis*(3,4-dihydro-3-methyl-2H-1,3-benzoxazinyl)isopropane and (2) based on the monomer 6,6'-*bis*(3,4-dihydro-3-methyl-2H-1,3-benzoxazinyl)sulphone are imported from Cerius²® into Materials Studio[®]. Molecular dynamics and molecular mechanical analysis are performed on both models with the aim of validating the results produced by Materials Studio[®] against previously recorded results from Cerius²® and empirical data.

Molecular dynamics results are obtained which are in reasonable agreement with empirical data. For instance, Materials Studio[®] predicts a T_g range of 188-196°C for polymer (1) which is within 11K of the empirical value of 177°C. Whereas, for polymer (2) a T_g of 133°C is predicted, which is within 16K of the empirical value of 117°C.

Similarly, molecular mechanics simulations produce some encouraging results, predicting a Young's modulus of 5.9GPa for (1), compared with the empirically measured value of 4.3GPa.

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RESEARCH PAPER

Validating software and force fields for predicting the mechanical and physical properties of poly(*bis*benzoxazine)s

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Similarly, molecular mechanics simulations produced some encouraging results, with a Young's modulus for (1) predicted as 5.9Gpa, compared to the empirically measured value of 4.3Gpa.¶

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1. Introduction

Poly(*bis*benzoxazine)s (sometimes simply referred to as benzoxazines) are a family of thermosetting polymers that are made by step growth ring opening polyaddition from *bis*benzoxazine monomers, which are themselves the products of the Mannich reaction between a *bis*phenol, formaldehyde and a primary amine ^[1].

Unlike many other thermosetting resins, which evolve condensation products such as water or ammonia, benzoxazine monomers react very cleanly to form a polymer without any reaction by-products ^[2]. The reaction used to make *bis*benzoxazine monomers can also yield a proportion of dimers and oligomers which can affect the properties of the resin before and during cure. The polarity of the solvent used in the reaction has a significant influence on the formation of dimers and oligomers, thus solvents of greater polarity assist bond formation between unreacted phenols and the heterocyclic benzoxazine ring, resulting in a greater yield of dimers and oligomers ^[1]. The monomer-oligomer ratio in the yield can also be influenced by using an excess of formaldehyde and amine during the synthesis. This alteration of stoichiometry causes the products to form *via* a different mechanism, resulting in a greater excess of monomer over dimers and higher oligomers ^[3]. Polymerisation of the monomer does not require the utilisation of strong catalysts, a characteristic with many advantages, *i.e.* not only is the material cost of the catalyst itself saved, but the manipulation of possibly highly corrosive media is avoided and possible damage to processing equipment is not an issue. Furthermore, the environmental impact from producing benzoxazines is considerably less than a polymer that would require a strong catalyst ^[3].

This paper will be concerned with the modelling of two poly(*bis*benzoxazines); the polymer made from 6,6'-*bis*(3,4-dihydro-3-methyl-2H-1,3-benzoxazinyl)isopropane (Figure 1a), which shall hereafter be referred to as (1) and the polymer made from 6,6'-*bis*(3,4-dihydro-3-methyl-2H-1,3-benzoxazinyl)sulphone (Figure 1b), which shall be referred to as (2). These two models were previously created in Cerius²® by Hamerton *et al.* ^[3] during an earlier piece of work to predict glass transition temperatures (T_g) and other mechanical properties including Young's Modulus. The simulations carried out in Cerius²® were carried out using the Dreiding Force Field. These modelling experiments have been repeated in Materials Studio[®] using the Universal Force Field (UFF) and the Polymer Consistent Force Field (PCFF) so that comparisons can be made between the two modelling packages and the force fields.

Dreiding and UFF are older forcefields than PCFF and are classified as class I forcefields. To calculate energies, they use general force constants and geometry parameters based on simple hybridization rules parameterised from experimental observations of vibration spectroscopy, gas-phase molecular structures, thermodynamic properties and crystal structures. However, class II forcefields (including PCFF) use tailored rules based on quantum mechanics for specific atom interactions ^[4-6]. The Dreiding forcefield is best suited towards molecules containing carbon, nitrogen, oxygen and hydrogen atoms, with only limited application within geometries, conformational energies, intermolecular binding energies and crystal packing. The Dreiding forcefield has recently fallen into disuse since the introduction of the more universally applicable class II forcefields ^[4-6].

The UFF is also a class I forcefield ^[6], it has been parameterized on element, hybridization and connectivity to cover the whole periodic table and has been validated for main group compounds, organic molecules and metal complexes. The downside of the UFF is that, with the aim of being able to simulate any system, it is not as accurate as a force field designed specifically for one class of molecule or compound. ^[6,7]

PCFF is an evolution of its predecessor, CFF91. It was designed to work well with polymers and organic materials such as polycarbonates, melamine resins, polysaccharides, lipids and nucleic acids with much validation work already carried out ^[6]. Advancing from the older class I forcefields, it can produce good results for cohesive energies, mechanical properties, compressibilities, heat capacities and elastic constants. It is worth mentioning that, although not used in the study, the Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies Force Field (COMPASS FF, a newer version of PCFF) is now considered a superior tool for working with polymer models ^[6].

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1.1 Modelling of Thermoset polymers

When thermosetting (*i.e.* network forming) polymers are considered for molecular modelling there are various constraints and approximations which need to be applied to make the task achievable. The most striking difference between network polymers and many of the other substances which are modelled is their sheer size. Unlike a drug, protein or linear polymer, it is impossible to consider the system as a discrete molecule as there is only one enormous molecule in a sample of network polymer. By far the most common method for modelling network polymers is to create a unit cell which could be considered representative of the polymer bulk. Then periodic boundary conditions are applied so the cell is modelled like a large sample and not a nanoparticle^[3,8-10]

Like many other network polymers, benzoxazines are amorphous, meaning they show no inclination towards crystallinity in the solid state, consequently representing their structure within a periodic cell could lead to inaccurate calculations. It can be considered though, that if the repeated unit cell is sufficiently large then the periodic crystallinity will be over such a large range as to be negligible. It can be very time consuming and difficult to create a cell of such size from scratch because there can be many hundreds of atoms that need individual placement and connection. One approach to simplify this task is to create a less complex cell containing a smaller number of monomer units. This cell is constructed in such a manner that multiple copies can be positioned adjacent to the first and bonds connected to make a single 'supercell'.

Although in the first instance this is creating crystallinity, a high temperature molecular dynamics simulation will allow the model to take on a more amorphous character because the individual cells within the supercell are allowed to behave differently and become random in their conformation and the effect of this can be seen in Figures 2a and 2b. The number and arrangement of unit cells used to make the supercell is obviously a careful consideration point. The size of the supercell is a simple trade off between computational resources and required accuracy. Clearly using a small number of unit cells will be less processor intensive, but will possibly return unusable results^[3]. On the contrary, too many unit cells can produce excellent results, but on a timescale which is impractical. With regards to the shape of the supercell, it is thought that a supercell with sides of equal length would be optimum, as this will maximise the distance in any direction before the cell is repeated.

Molecular modelling can be used to determine several properties about polymers by simulation and calculation. Of these, perhaps the most important are the T_g and the Young's modulus, since these relate to the potential technological application of the material^[8]. The importance of T_g lies in its importance in determining the temperature range in which the polymer can be processed and utilized^[8]. Thus, being able to determine the T_g of a novel polymer by computational methods would be a great benefit when screening candidate structures for further investigation. Instead of calculating the glass transition temperature from parameters, the molecular dynamics method can be utilized with a molecular model to estimate T_g ^[31] without such extensive knowledge of the polymer chemistry. Molecular dynamics (MD) will simulate the location and velocity vector for each atom within the model over time under specified conditions. This method can be used to calculate T_g by running simulations at various temperatures and taking readings for volume. These data can then be used to plot a graph and T_g can be estimated as the point of intersection between the thermal expansion gradients for above and below the glass transition temperature^[9]. To find the two thermal expansion gradients the data sets will need to be sub-divided into two groups, for above and below T_g , but naturally at this stage the T_g is unknown. This requires a number of possible graphs to be drawn up, each splitting the data at a different temperature. This set of graphs can then be compared visually and by correlation coefficients to determine which should be used to define the range of T_g .

From these graphs the volume thermal expansion coefficient (α) can be calculated from the gradient using Equation 1.

$$\alpha = \frac{1}{V} \left(\frac{\delta v}{\delta T} \right)_p \quad (1)$$

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Deleted: . The importance of T_g is because it determines the temperature range in which the polymer can be processed and utilized^[4]. The calculation of T_g can be done in a number of different ways, three of these shall be discussed in the order: group interaction modelling, atomic additivity and molecular dynamics.¶

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Where V is volume, T is absolute temperature and the system is barostatic at pressure P. The volume thermal expansion coefficient is useful in molecular modelling because it can be compared with literature or experimental data for the material as a means of validation^[9, 11]. It should be noted however, that MD simulations can be very computationally intensive, and accurate results can sometime take weeks or months to produce^[3].

Young's modulus is a measure of the stiffness of a material and is an important property to consider when choosing a material for a specific application. The modulus of a material can be calculated from the molecular structure using the Discover module in Materials Studio[®]. The objective of these small scale simulations is to reproduce the observed mechanical properties, by this means the process can then be made truly predictive. The ultimate aim of simulation is to ensure that there are no motions in the bulk sample that are not reproduced in the model.

2. Computational Methodology

Two computers were used for this work, a client PC running Materials Studio[®] (Accelrys Software Inc.) under a Windows environment and a server for processing the calculations. The server was using a dual core, Intel Pentium D CPU 3.40GHz processor running at 2289 MHz with 2016Mb of RAM and a Linux operating system.

The molecule files used in this study were previously created in Cerius^{2®} using the Dreiding forcefield. Initially, a two-dimensional model of each monomer was constructed using the 'crystal builder' module in Cerius^{2®} (using the three dimensional, 3-d, builder module) on an atom-to-atom basis to form a bis-benzoxazine dimer with explicit hydrogen atoms and with each benzoxazine ring left as a non-bonded group. Energy minimisation was performed on this molecule using the second derivative method until it achieved convergence to an RMS force of 0.01 kcal mol⁻¹. Three further monomers were added to form a pentamer and this structure (termed a single 'unit cell') was minimised until convergence, again to an RMS force of 0.01 kcal mol⁻¹. In order to apply periodic boundary conditions, periodic cells were constructed in which the oligomeric chains contained within the cells were 'manually' linked together by breaking and forming the appropriate bonds, thus forming a 'crosslinked', 3-dimensional network. Thus, two cells were visualised in the x-axis by moving necessary bonds close to one another and removing cell boundaries and the 3-d lattice was then built up by connecting the nitrogen atoms on non-bonded benzoxazine rings and non-bonded carbon atoms in the benzoxazine dimer, across the x, y and z directions of the structure. At each stage the growing group of unit cells were subjected to energy minimisation so the energetically optimised conformation of the polymer was obtained. Additional unit cells were added to make a 3D model (i.e. a super unit cell comprising 27 individual units)^[3]. These molecule files were in the format used by Cerius^{2®} and needed to be imported into Materials Studio[®], this was done using Materials Visualizer, a constituent of Materials Studio[®].

The geometry was then optimized using Materials Studio[®]'s Forcite module with the following settings:

- Universal Force Field with default settings;
- Ewald summation for Van Der Waals forces;
- dynamic cell dimensions and angles;
- smart algorithm, which is a cascade of the steepest descent, Adopted Basis Newton-Raphson, and quasi-Newton methods;
- maximum iterations unlimited;
- "Ultra fine" convergence tolerance
 - < 2*10⁻⁵ kcal/mol energy variance;
 - < 0.001 kcal/mol/Å Force variance;
 - < 1*10⁻⁵ Å displacement variance.

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Once the cell geometry had been optimised, molecular dynamics simulations were carried out for the prediction of glass transition temperatures using the Forcite module running the 'Universal force field' on Medium quality. Van der Waals forces were controlled by Ewald summation. The simulation was run as an NPT ensemble, keeping the number of atoms, pressure and temperature constant. Although the volume of the cell could change, the cell angles and hence the shape were fixed, unlike an NVT ensemble, where the volume and shape of the cell are kept constant. An external pressure of zero was barostatically maintained. The simulation was run for 25 picoseconds with a 1 femtosecond time step, temperature was controlled by the Nosé thermostat (Q ratio = 1.0) and pressure was controlled by the Berendsen barostat (decay constant = 0.1ps).

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To predict T_g , MD simulations were run at the following temperatures in the order shown: (temperatures measured in degrees Celsius),

- (1) 427, 327, 277, 252, 227, 202, 177, 152, 127, 102, 77, 27,
- (2) 427, 327, 277, 227, 202, 177, 152, 127, 102, 77, 52, 27, -23, -73,

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The simulation was continuous, with the final state of the previous simulation trajectory used as the start state for the next.

The Young's modulus and other elastic properties were calculated using the static elastic properties analysis within the Discover[®] Module using the PCFF at medium quality. This analysis is performed on a single conformation of the model at 0°C, and the program will return values for the elastic properties without a need for further calculation.

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3. Results and discussion

The results from the simulations are displayed in Figures 3a and 4a with standard deviation error bars and best fit thermal expansion gradients for above and below T_g . It is worth noticing the results from the 427°C simulation were left out from the thermal expansion gradient calculation because at this temperature the polymer may well be involved in a transition separate from the glassy – rubbery transition. This step was still important from the perspective of the whole simulation though because it helped to give the model more amorphous character. The low temperature points were also excluded from the results because it was desired to base the best fit line on the results we had confidence in belonging to the linear part of the volume-temperature curve.

3.1 Analysis of Polymer cured from 6,6'-bis(3,4-dihydro-3-methyl-2H-1,3-benzoxazinyl)isopropane (1)

To determine T_g from the data, two best fit lines must be drawn, one representing the thermal expansion below T_g , and one representing thermal expansion above T_g . The point at which to make this cut-off is typically not known, and so several different possible cut-off points were tried. This set of graphs is analysed visually, and the R^2 correlation coefficients were used to accurately find the point of gradient change. From these trials, the intersection points of the best graphs were taken to give two possible T_g values, 188°C and 196°C, with greater confidence in the prediction of 188°C from R^2 correlation coefficients (Table 2). This can be considered as a T_g point of 188°C or more correctly, a T_g range of 188°C – 196°C.

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The cut-offs that gave rise to a predicted T_g of 188°C displayed a higher R^2 correlation coefficient product which means higher confidence in the data, hence it was chosen for comparison with previous work conducted by Hamerton *et al.*¹³¹(Figures 3a and 3b). The comparison of these two graphs shows a very close similarity in T_g values, with the intersection for the new data at 188°C compared with a temperature of ca. 180°C from the older work.

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It can be seen from the graphs that quite different temperature regimes were investigated. The earlier experiments were taken over a broader temperature range of 600K with points generally 50K or more apart,

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whereas the recent work focused attention over a range of 300K with points generally 25K or more apart. This new approach was considered an improvement as more data were obtained closer to T_g , where they are more relevant. Furthermore, when the temperature deviates greatly from T_g the polymer will be involved in other transitions which will disrupt the linear thermal expansion which is required to obtain an accurate intersection point.

Although the R^2 correlation coefficients and standard deviations were not calculated for the previous work, a visual inspection of Figures 3a and 3b clearly shows how Materials Studio[®] yields results that are more self-consistent than those calculated by Cerius^{2®}.

The simulation data for (1) can be compared with the empirical differential scanning calorimetry (DSC) data obtained in previous work^[3]. The T_g of 188°C determined in the simulation is quite comparable with the DSC T_g range of 163 – 177°C (10K min⁻¹ heating rate; 5 min isothermal hold at 250K; cooling at -10K min⁻¹). A common feature of simulations in recent and previous work is the predicted T_g is higher than the empirical value for T_g . It is thought that the defect filled amorphous structure of the cured plastic containing solvent molecules and unreacted groups will have a lower T_g than the defect free, slightly crystalline structure (an artificial construct) which is actually being modelled. This discrepancy between the physical material and the molecular model is something that will need to be addressed if the accuracy of the results is to be improved.

The density of the models at 0°C as predicted by Materials Studio[®] (1.03 g/cm³) and Cerius^{2®} are both lower than the empirically measured value of 1.12 g/cm³^[11] (Table 1). The reason for this lower than expected density could be explain by the fully cured and slightly crystalline model, allowing cavities to be held open by the structure, whereas a true sample would have a little more freedom, allowing it to pack more tightly. It could also be true that impurities such as solvent molecules and moisture (which are not represented in the models) could pack in the cavities, increasing the mass without significantly affecting the volume.

Materials studio[®] also has the ability to calculate effective isotropic elastic constants from a molecular model and these are displayed with the constants that were calculated by Cerius^{2®} and empirical data from Ishida *et al.* in Table 1. Although the data are in the right vicinity, with both programs producing parameters in the GPa range, the correlation is not sufficiently close to make effective use of these data, with the obvious exception of Poisson's ratio. Unfortunately, there is not a large amount of empirical data available for these materials which could be used to verify which modelling software attained the more accurate results. There was, however, an empirical value for the Young's modulus of (1) and, although it would be preferable to compare a number other cell parameters as well, it would suggest that Materials Studio[®] is producing notably more accurate results. The slightly higher result for Young's Modulus over the empirically measured value is to be expected for the same reason that the T_g values were high, the defect free system will always be stronger than actual material which cannot cure to a 'perfect', fully crosslinked structure.

3.2 Analysis of Polymer cured from 6,6'-bis(3,4-dihydro-3-methyl-2H-1,3-benzoxazinyl)sulphone (2)

The methods for analysing and processing the data for (2) were the same as those used with (1). The data can be considered to represent a T_g range of 133°C – 167°C with the point of gradient change more likely at 167°C. The comparison of the best fit for the recent work with the previous work (Figures 4a and 4b) can be considered in two different ways. The initial impression is that the two graphs do not show an overwhelmingly good correlation, and this may be so, with the old T_g prediction of 130°C being a significant 37K lower than the recently predicted T_g of 167°C. However, if the two sub-ambient temperature results are omitted from Figure 4b, for the reasons mentioned previously, the two graphs would have similar distributions of data.

Comparison of DSC thermogram results show a T_g of 117°C^[3] with simulation data predicting a T_g of 167°C (Figure 4a) for (2), this is not as encouraging as the same comparison as with (1). It would perhaps

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be useful at this stage to consider that the simulation data could also be used to show a prediction of 133°C (If different cut-off points are used to separate data into $<T_g$ thermal expansion and $>T_g$ thermal expansion). Although this interpretation was not chosen as the best analysis of the data, it still has a high R^2 correlation coefficient, indicating a close fit. It is thought that the analysis of (2) will require better resolution between 50°C and 250°C to help narrow down the predicted T_g range.

Although there is no empirically-measured value for density, it is interesting to note the similarity between the density predicted by Materials Studio[®] and Cerius^{2®}. Unfortunately, the density results for (1) do not show such close correlation, and so we cannot conclude that the two programs will always equilibrate the same model to the same density.

The effective isotropic elastic constants for (2), as calculated by Materials Studio[®] and Cerius^{2®} are shown in Table 1. Although there are no empirical data available for (2) specifically, if the Young's moduli of epoxies (~2.6 GPa), phenolics (4.1 – 8.4 GPa) and melamine polymers (~8.9 GPa) are considered, it can be theorised that the values produced by Materials Studio[®] are likely to be closer to the empirically measured value^[12].

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4. Summary and Conclusions

Two molecular models were imported into Materials Studio[®] from previous work conducted at the University of Surrey. These models were individually geometry optimised and then used in molecular dynamics simulations to predict the glass transition temperatures of both materials. A range of mechanical properties were also calculated, including bulk modulus, Young's modulus, Poisson's ratio and the Lamé constants, λ and μ .

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The new data produced in Materials Studio[®] have varying compatibility with previous data from Cerius^{2®}. The main emphasis of this work was with regards to predicting glass transition temperatures, and it is within this area that the best results were achieved. The predictions are high in comparison with empirical data, but this is to be expected with defect free systems, and it is clear to see how the model can be improved by adding defects in the structure so it is more consistent with a natural system. The same explanation can be given for why the Young's modulus predicted by Materials Studio[®] is slightly higher than the empirically measured value.

The effective isotropic elastic constants do not compare very well between Materials Studio[®] and Cerius^{2®}, with calculations giving quite different results. Although there is not a wealth of empirical data with which to compare these figures, from what is available, it is encouraging to see that Materials Studio[®] does appear to be producing the more accurate results.

4.1 Further Work

It is clear that there is still much room for improvement within the methods used to predict the glass transition temperature and mechanical data. Obviously, it would be ideal to run simulations on supercells with nanometre length sides for a number of nanoseconds using the best levels of precision available within the choice of force-fields. However, these experiments will always be limited by the processing power available and such an experiment would take many years even on a high-end supercomputer. It would be advisable to begin any further work by determining the most efficient use of processing power by applying principal components analysis or a similar statistical technique to the many variables. By doing this the optimum settings can be determined under which to run the simulation.

One factor that has been mentioned already during the report is the temperature range over which the experiments are conducted. Molecular dynamics is used to simulate an experiment which is normally undertaken between ambient and ca. 300°C, however the simulation carried out in the previous work ranged from -173°C to 427°C and the recent work from -73°C to 427°C. If the simulations are conducted in the

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temperature range over which the physical experiment is more traditionally performed the results would surely be more representative of the empirical data attained from said experiment.

Although investigations into the use of larger supercells were limited to one trial, the results are worthy of note because it was the only factor which significantly reduced the standard deviation of the cell volume. Certainly, if more powerful computing resources are made available it would be beneficial to utilise a 4x4x4 unit supercell in molecular dynamics simulations.

It was mentioned in the discussion of the results how the defect free benzoxazine model will always have higher values for glass transition temperature and Young's modulus. In future work it would be an improvement to the model if a number of defects and solvent molecules were introduced into the molecule to make it more representative of the true polymer. Although previously it was difficult to navigate within the large supercell to introduce such defects, recent work with 3D visualisations has allowed modifications within the supercell to be made with great ease and this forms the basis of current work.

We have adopted a number of these more advanced ideas into the evolution of our thermoset modelling technique^[13].

5. References

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Legend to Figures

Figure 1a – 6,6'-bis(3,4-dihydro-3-methyl-2H-1,3-benzoxazinyl)isopropane monomer.

Figure 1b – 6,6'-bis(3,4-dihydro-3-methyl-2H-1,3-benzoxazinyl)sulphone monomer.

Figure 2a – Molecular model of (1) before high temperature molecular dynamics.

Figure 2b – Molecular model of (1) after high temperature molecular dynamics.

Figure 3a – Change in cell volume with temperature from recent work with (1), showing standard deviation with error bars.

Figure 3b – Change in cell volume with temperature from previous work with (1).^[3]

Figure 4a – Change in cell volume with temperature from recent work with (2), showing standard deviation with error bars.

Figure 4b – Change in cell volume with temperature from previous work with (2).^[3]

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Table 1. Summary of data

Parameter	Materials Studio®		Cerius ² [31]		Empirical Data [3, 11]	
	(1)	(2)	(1)	(2)	(1)	(2)
T _g range (°C)	188-196	133-167	-	120-150	-	-
T _g point (°C)	188	167	180	130	177	117
Density (g/cm ³)	1.03	1.14	0.93	1.15	1.12	-
Bulk Modulus (GPa)	4.12	3.37	36.3	17.6	-	-
Poisson's ratio	0.29	0.31	0.29	0.23	-	-
Lamé constant λ (GPa)	2.75	2.40	24.5	15.7	-	-
Lamé constant μ (GPa)	2.06	1.46	23.6	11.0	-	-
Young's modulus (GPa)	5.92	3.82	48.0	30.0	4.3	-

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 Table 1. Isotropic elastic constants for (1). [1]

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 Table 2. Isotropic elastic constants for (2). [2]

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Table 2. R² Data for best fits

R ² Values	Below T _c	Above T _c
(1)	0.958	0.963
(2)	0.989	0.994

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Other information

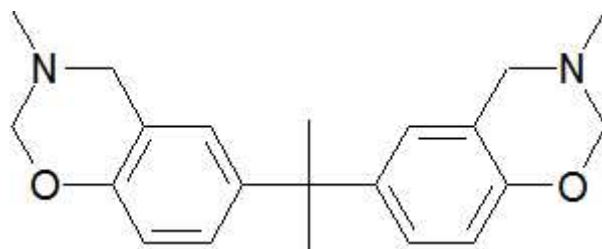
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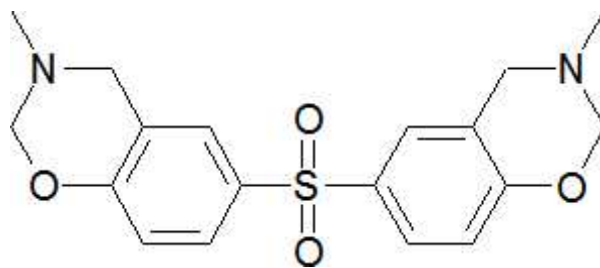
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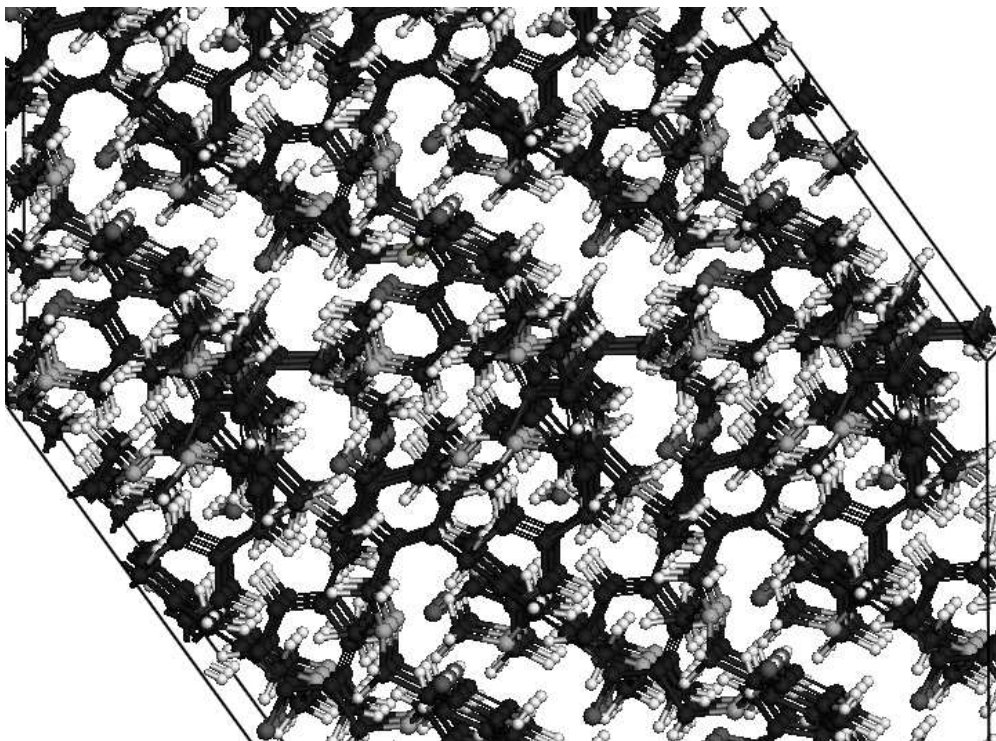


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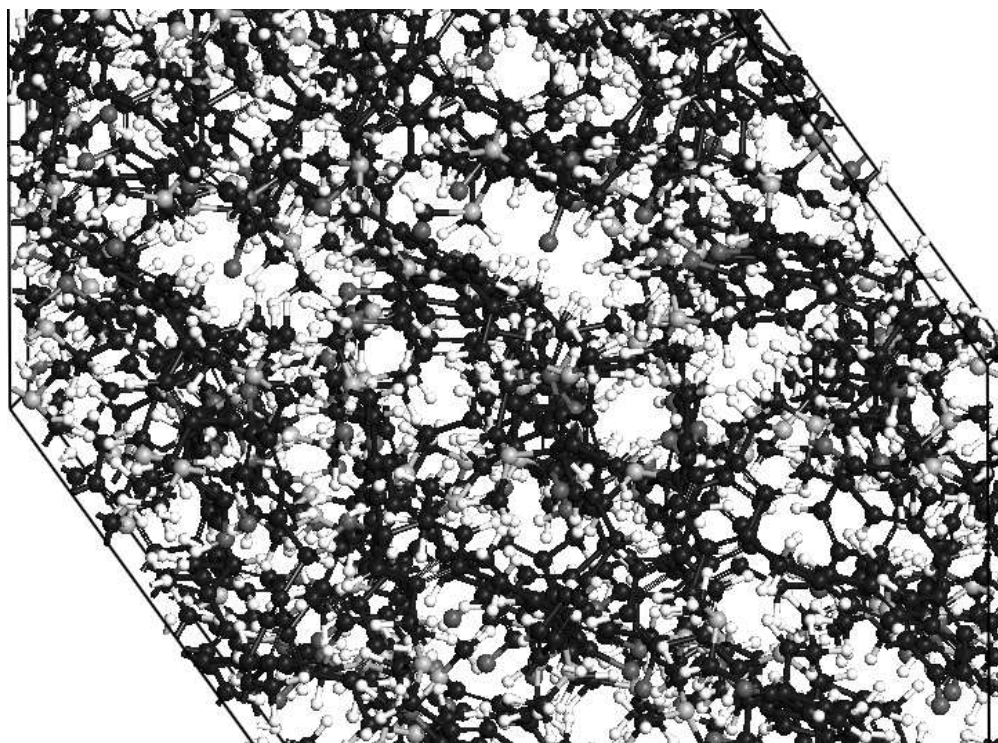


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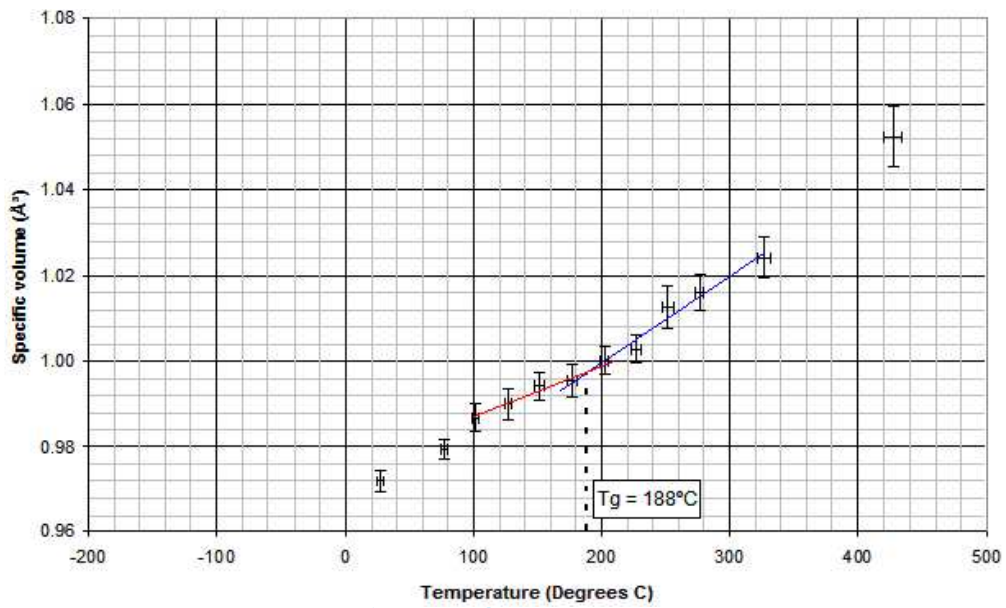
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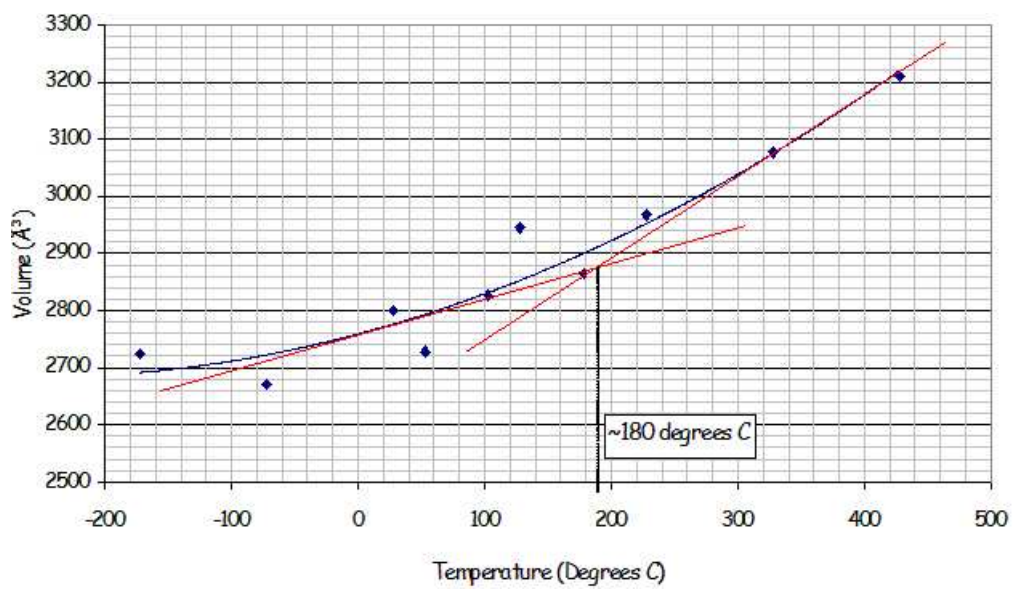
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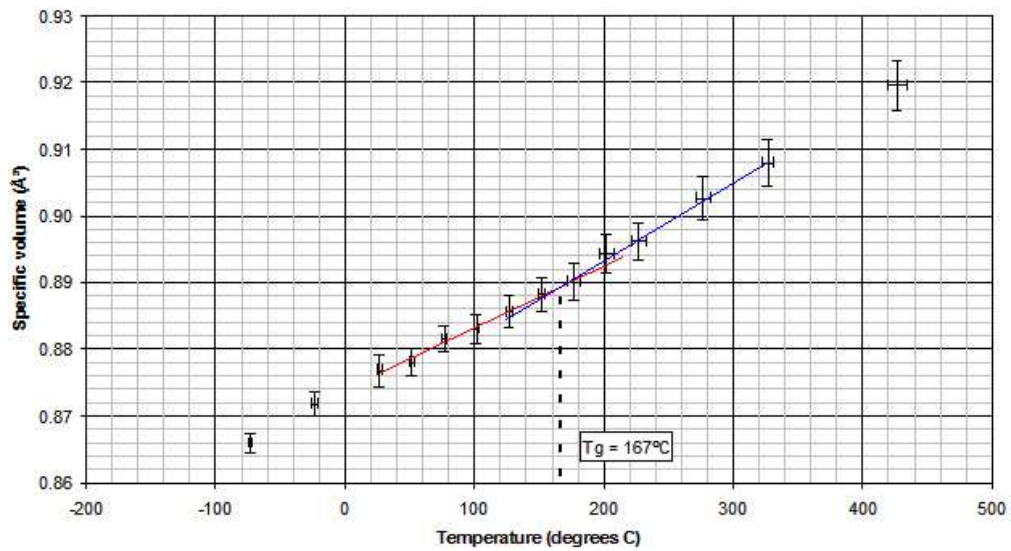


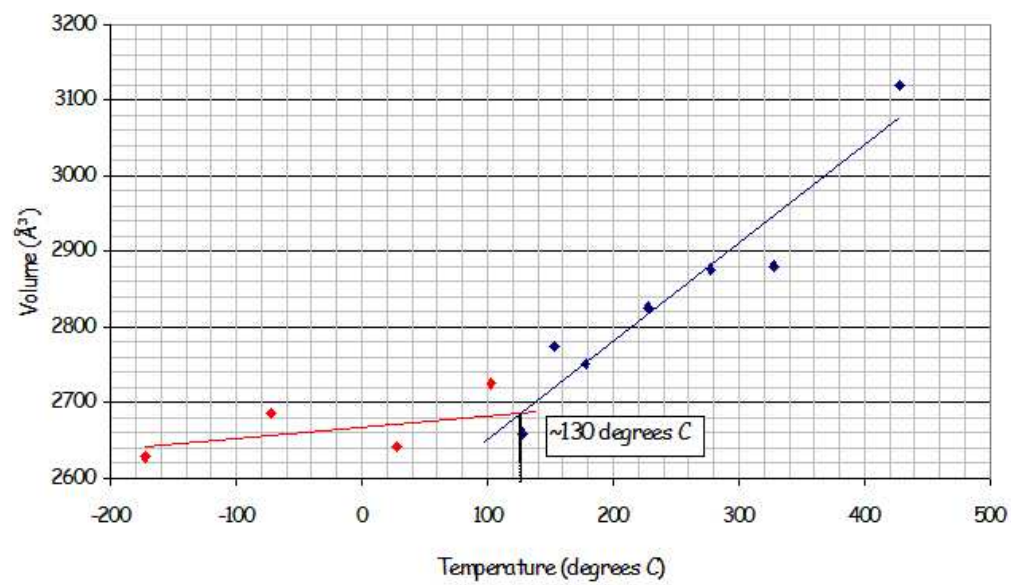
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