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Developing predictive models for polycyanurates through a comparative study of molecular simulation and empirical thermo-mechanical data

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Abstract

Using a parameter set (RDA-DR2.21_Inv) previously published by our group, both the atom-to-atom connectivities and geometries and the physical and mechanical properties of poly[bis-4-(4-cyanatophenoxy)phenyl sulphone] have been simulated with remarkable accuracy. Molecular dynamics simulation, carried out on the polymer structure at a variety of experimental temperatures, yields a transition temperature of ca. 510–520 K, which can be equated with the empirical glass transition temperature (T_g) for the polycyanurate. The same dicyanate was prepared experimentally and characterised using dynamic mechanical analysis (yielding an empirical T_g of ca. 519 K) and thermo-mechanical analysis (yielding an empirical T_g of 508–528 K). The effect of incomplete cure of the monomer or development of structural defects in the network on the thermo-mechanical properties is also examined using molecular simulation.
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1. Introduction

Cyanate ester resins (polycyanurates) are a family of thermosetting resins that are used within a variety of electronic and microelectronic applications. Once cured, polycyanurates offer high performance, including relatively high glass transition temperature ($T_g = 463–563$ K, depending on structure and degree of cure), high fracture toughness (typically $G_{IC} = 140–225$ J m^{-2}, although this can be raised significantly by blending with engineering thermoplastics) and good hot/wet performance [1]. Currently, the single largest application for polycyanurates is as lamination substrates for printed circuits and their assembly via prepreg adhesives into high-density, high-speed multi-layer boards, which are produced commercially for supercomputers, mainframes and high speed workstation mother units [2]. Polycyanurates also develop interesting dielectric properties (typically, the dielectric constant is 2.2–2.7 and the dissipation factor is 0.003 at GHz frequencies) that make them particularly attractive in these applications, for which epoxy resins and polyimides are market contenders.

Polyfunctional cyanate monomers cure via the formation of cyanurate rings (*sym*-triazine rings linked by aryl ether linkages to a polymer, correctly termed a polycyanurate) and a simplified reaction is depicted in Scheme 1 for bis-4-(4-cyanatophenoxy)phenyl sulphone (catalyst packages typically comprise a transition metal carboxylate or chelate and an alkyl phenol).

Although this reaction scheme predominates during the polymerisation, it is now recognised that the earlier claims for the exclusive formation of cyanurate rings [3] were somewhat optimistic and there is still debate about the exact nature of the polymerisation mechanism. Many routes have been proposed to acknowledge the effects of different catalysts and reaction intermediates—a fuller discussion of this aspect is outside the scope of the current paper although the reader is directed to other sources [4–8] in which this is dealt with in some detail.

For almost 15 years, research at Surrey has examined, with some success, how synthesis might yield polycyanurates (and indeed many other engineering polymers) with superior

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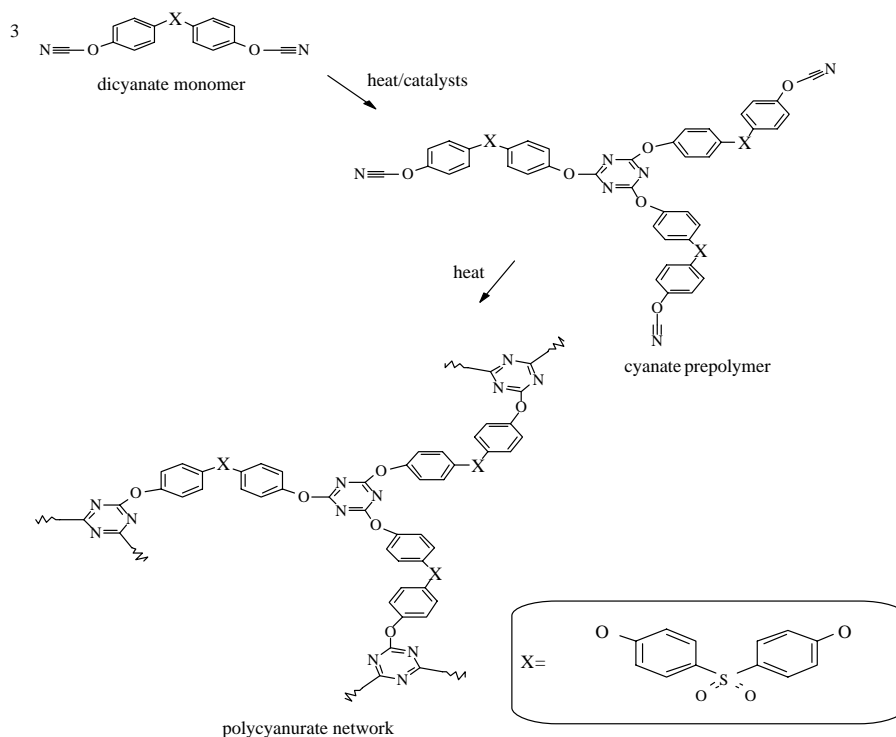
Scheme 1. Simplified cyclotrimerisation reaction to produce polycyanurate network (shown for bis-4-(4-cyanatophenoxy)phenyl sulphone).

properties to existing polymers, or how chemical modification might be employed to increase the utility of commercial dicyanates. During this time, many monomers, blends and copolymers have been prepared (on a variety of scales) through the efforts of a team of researchers, characterised and tested for their physical and mechanical properties. This effort has, of necessity, involved many chemicals, much analysis time and the involvement of many laboratory hours 'at the bench'. In common with 'traditional' chemical synthesis involving the preparation of 'small' organic molecules, polymer synthesis brings many similar challenges and a few additional problems (e.g. limited solubility or reduced reactivity) arising from the extended chain structure. However, no matter what the nature of the preparation (whether fine chemicals, pharmaceuticals, agrochemicals or polymers), every synthesis will require that reaction conditions (e.g. temperature, solvent, pressure, reagents, and catalysts, etc.) are optimised. Furthermore, every preparation will consume energy and feedstock materials and generate waste (in the form of gaseous emissions, solvated (by)products or solid matter—the latter may be the desired product, but might also be accompanied by contaminants. It is self evident that energy requirements should be recognised for their environmental and economic impacts and to reduce them accordingly and that the prevention of waste is preferable to the treatment or clean-up of waste after it has formed.

Anastas and Warner have discussed, at length, the role that chemistry has in reducing the impact of chemicals and chemical processes on the environment and as a result have formulated their '12 principles of green chemistry' [9]. Recently, a 13 principle was mooted [10] namely that 'where possible, the reliable simulation or prediction of materials properties should be employed to optimize synthesis and reduce its impact on the environment'. The increasing advances made in computational power make the use of simulation techniques increasingly useful in the rational design of new materials. By adopting much of the methodology piloted with great success by the pharmaceutical industry to model the interaction of drug molecules with the active sites of proteins [11], molecular modelling has become generally accepted as a powerful technique for understanding some of the properties exhibited by materials. While still in its infancy in the field of polymer chemistry, computational chemistry has the potential to simulate the properties of novel materials, as yet unsynthesised. There is also the possibility of employing molecular simulation in a predictive capacity potentially offering savings in both labour and cost and reductions in chemical waste. Ultimately, this would allow the scientist or engineer to examine the potential of a novel structure to give him or her the required properties (e.g. heat resistance, bulk modulus or glass transition temperature) to fulfil a new application, without having to prepare the actual material in the laboratory. For although computation experiments do consume energy, the additional burdens, which synthesis places on the environment, would be largely avoided or dramatically reduced. At a later stage, the new monomer or polymer would be prepared in order to allow small scale testing, prior to scale up, but extensive exploratory syntheses to develop many potential monomers would be unnecessary.

A laudable aim, but how realistic is this aspiration? In 1996, Boyd published [12] a useful review detailing the state of the art (at that time) for the simulation of the glass transition from molecular dynamics simulations. He concentrated on

engineering thermoplastics, but the simulation of linear and branched thermoplastics is conceptually simpler to achieve (than e.g. thermosetting polymers) and can yield good correlation with empirical data [13,14]. The simulation of network-forming polymers is necessarily somewhat more difficult in view of the structural complexity and the need to produce a representative model structure. Having published an early study to examine the thermo-mechanical properties of a polycyanurate [15] involving a rather crude model, albeit advanced for its time, we now present a more sophisticated model. In this paper we examine the effect of network defects on the behaviour of a well-characterised polycyanurate. The results of the simulations will be compared to empirical thermal and mechanical data.

2. Experimental section

2.1. Materials

The details of the preparation and characterisation of bis-4-(4-cyanatophenoxy)phenyl sulphone (see monomer structure in Scheme 1) are reported elsewhere [16]. It is worth noting that the combination of analytical techniques confirmed that the monomer had been produced in good yield and high purity (a purity of 98.4% was recorded by HPLC).

2.2. Procedure for blending of the dicyanate and co-catalysts and cure schedule employed to effect cure

Prior to incorporation in the dicyanate, the co-catalyst package, comprising aluminum(III) acetylacetonate and dode-cylphenol in the molar ratio of 1:25, was first homogenised by heating to 353 K (in a vial in a water bath) before cooling to room temperature. The co-catalysts were then introduced into the dicyanate monomer (typically at a molar ratio of aluminum(III) acetylacetonate/dodecylphenol/monomer of 1:25:1000) by mixing in a pestle and mortar at room temperature to a homogeneous mixture. The ensuing formu-lations were used in the thermal analyses directly after incorporation of the co-catalysts. Storage of catalysed formulations was undertaken in a refrigerator (<278 K) with care being taken to minimise the exposure of the sample to atmospheric moisture. Prior to the dynamic mechanical analysis (DMA) and thermomechanical analysis (TMA) measurements, the catalysed monomer was cured thermally by application of the following cure schedule: 423 K (1 h), 453 K (5 h) and 503 K (5 h).

2.3. Apparatus

Fourier transform infrared (FT-IR) spectra were recorded using a Perkin–Elmer (system 2000 FT-IR) spectrometer interfaced with a PC running PE-spectrum v 2.00 software. The samples were presented on an ATR module, 16 scans, at a resolution of 4 cm^{-1}, were recorded and co-added to produce the final spectrum. Dynamic mechanical analysis measure-ments were undertaken in tensile mode at a frequency of 1 Hz

(6.28 rad s^{-1}), on cured neat resin samples of $5 \times 0.5 \times 35$ mm^3 using a Rheometrics solids analyzer RSA II with a Rheometrics environmental controller unit. Scanning exper-iments were performed between 123 and 623 K at a heating rate of 5 K min^{-1}. Thermomechanical measurements were undertaken using a Seiko Instruments, Inc. EXSTAR6000 TMA/SS6000 on cured neat resin samples of between 0.7 and 1.1 mm thickness. A probe weight of 0.5 g (4.9 m N) was used on an analysis area of 9.026 mm^2, while being scanned at a heating rate of 5 K min^{-1}. The density the cured polymer sample was measured using Archimedes' principle (by measuring displacement of fluid from an immersion tank) at 298 K using a Mirage Trading Co., Ltd. SD200L electronic densimeter.

2.4. Modelling methodology

Molecular simulations of the polycyanurate were performed using a Silicon Graphics Origin 2000 multiprocessor machine termed 'Proton' at the UK Computational Chemistry Facility at The Rutherford Appleton Laboratory. The calculations ran under Irix 6.3 with the Cerius^2 (Accelerys, Inc.) software package. Energy minimisations were achieved using a modified Dreiding v.2.21 force field (RDA-DR2.21_Inv), previously reported for similar polycyanurate structures [17], in conjunction with the Qeq charge calculation [18].

2.5. Molecular mechanics (MM) study

The dicyanate monomer, bis-4-(4-cyanatophenoxy)phenyl sulphone is shown in Scheme 1. Initially, a two-dimensional model was constructed (using the three-dimensional, 3-d, builder module) on an atom-to-atom basis to form a *sym* triazine ring with explicit hydrogen atoms and with each *O*-substituent left as a non-bonded cyanate group (i.e. to form the molecule tris(4-cyanatophenoxy-1,3,5-triazine)). Energy minimisation was performed on this molecule using the conjugate gradients routine achieved convergence to an RMS force of 0.01 kcal mol^{-1}. Three more triazine rings were added, each with two bonded carbon atoms in the triazine ring and one free carbon atom, allowing the three pairs to be bonded when the 3-d structure was built. This structure was minimised until convergence, again to an RMS force of 0.01 kcal mol^{-1}. In order to apply periodic boundary conditions (PBC), two cells were visualised in the *x*-axis by moving necessary bonds close to one another and removing cell boundaries. The 3-d lattice (Fig. 1) was then built up by connecting the three pairs on non-bonded cyanate groups and non-bonded carbon atoms in the triazine rings, across the *x*, *y* and *z* directions of the structure. This was the starting point for the energy minimisation in the MM studies.

Periodic cells were constructed and three cycles of 10 ps molecular dynamics and 100,000 steps of energy minimisation were then performed to reach an optimum density for the monomer. Density, volume and cell dimensions, were calculated for the molecule (Table 1) and the bond distances and angles presented in Table 2 for the dicyanate monomer.
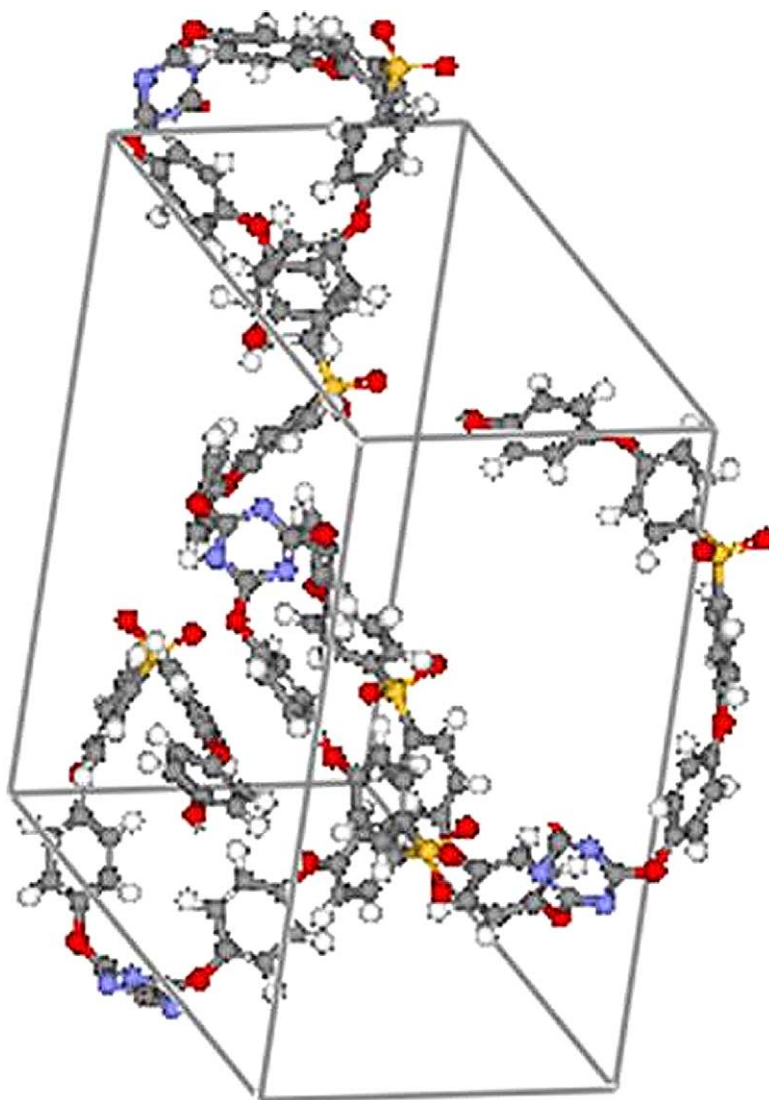
Fig. 1. 'Unit cell' of bis-4-(4-cyanatophenoxy)phenyl sulphone (NB, oxygen atoms are shown in red, nitrogen atoms in blue, sulphur atoms in yellow, carbon atoms in black and hydrogen atoms in white) (For interpretation of the reference to colour in this legend, the reader is referred to the web version of this article).

Table 1

Summary of data derived from Cerius^2 experiments for bis-4-(4-cyanatophenoxy)phenyl sulphone) (for a given structural conformation)

Cell parameters	
Density (g/cm^3)	1.20
Volume (Å^3)	4031
Dimensions (Å)	
a	13.86
b	22.36
c	15.75
Angles (°)	
α	120.34
β	81.65
γ	84.21
Mechanical properties	
Bulk modulus (GPa)	4.37
Young's modulus (GPa)	3.38
Poisson ratio	0.38

2.6. Molecular dynamics (MD) study

The MD module in Cerius^2 was used to simulate the glass transition temperature (T_g) by monitoring changes in cell volume, while keeping the number of atoms present, pressure and total energy constant. The volume change at a specified temperature was recorded after a period of 250 ps simulation

Table 2

Bond distances and angles of the *sym* triazine ring for the polycyanurate of bis-4-(4-cyanatophenoxy)phenyl sulphone obtained using the RDA-DR2.21_Inv forcefield (for the given conformation)

	Bond distances (Å)	Bond angles (°)	
	C–N	C–N–C	N–C–N
Mean[a]	1.336	112.25	127.72
Cyclotrimer[b]	1.341	110.34	124.10

[a] Average crystal data [from Ref. [17]].
[b] Data represent cyclotrimer of bis-4-(4-cyanatophenoxy)phenyl sulphone.

steps. Simulations were initially conducted at 700 K and thereafter at 100 K intervals to a minimum of 200 K and changes in cell volume were plotted against the entire working range of temperature.

3. Results and discussion

During the last decade, several groups have reported results from conformational studies of the *sym* triazine ring structure (and many fragments containing *sym* triazine rings) by means of computer modelling. There have also been some previous studies by our group involving molecular modelling of polycyanurates [15,19] as well as some studies of network build up in the same polymers conducted by other researchers [20,21]. However, this paper represents a new and exciting step in this process. Our work has been advancing towards the reliable prediction of physical and mechanical properties in polymers from molecular simulation. In this way the decision might be made whether the synthesis of a novel monomer (or untested polymer) might be worthwhile to achieve a particular set of performance characteristics. To this end, in a previous paper [16] we reported a molecular simulation study of three commercially available polycyanurates. The materials, 2,2-bis(4-cyanatophenyl)propane (available commercially as AroCy B-10), 1,1-bis(4-cyanatophenyl)ethane (AroCy L-10) and 1,3-bis(4-cyanatophenyl-1-(1-methylethylidene))benzene (XU 366), were selected on the basis that they were well known and their physical and mechanical characteristics had been well documented in the literature. These were selected in order to validate the parameter set that we have employed in this work. Naturally, it should be borne in mind that a study of this kind cannot indicate whether a proposed molecule can be synthesised, only whether it would have desirable properties if it could be synthesised.

3.1. Molecular mechanics data

The unit cell data (derived from Cerius^2) for the polycyanurate are given in Table 2. The calculated density for bis-4-(4-cyanatophenoxy)phenyl sulphone is 1.20 g cm^{-3}, compared with the empirical density of the cured polymer of 1.34 g cm^{-3}. The empirical value was measured at 298 K, whereas the simulated value is given at 0 K. This difference is related to temperature as the simulated value lies in the range of 1.31–1.34 g cm^{-3} during molecular dynamics at 300 K.

3.2. Molecular dynamics data

It is well known that the structure of thermosetting polymers is spatially heterogeneous, containing both amorphous and crystalline regions. Naturally it is impossible to model to this degree of structural accuracy with a model based on periodic boundary conditions. The model used represents in essence a snapshot of an essentially crystalline section of the polymer. Hence values of T_g that are derived from the simulation should represent the higher end of the experimental T_g determinations as amorphous regions tend to lower the T_g. Cyanurate thermosets show a high degree of conversion experimentally, in the high 90's of percent conversion, so a regular model with many cyanurate rings is actually a very good representation of the structure of the cured polymer in this case, as the high degree of bonding to form the cyanurate rings is coupled with limited flexibility about the connecting branches.

The empirical determination of T_g from changes in specific volume is accepted as a useful method in the analysis of thermomechanical properties in polymers [22], although a gradual change in physical state is observed yielding a marked change in gradient. MD simulations were carried out on poly[bis-4-(4-cyanatophenoxy)phenyl sulphone] in order to calculate the T_g of the polycyanurate. The results from the initial molecular dynamics run (comprising six experiments at
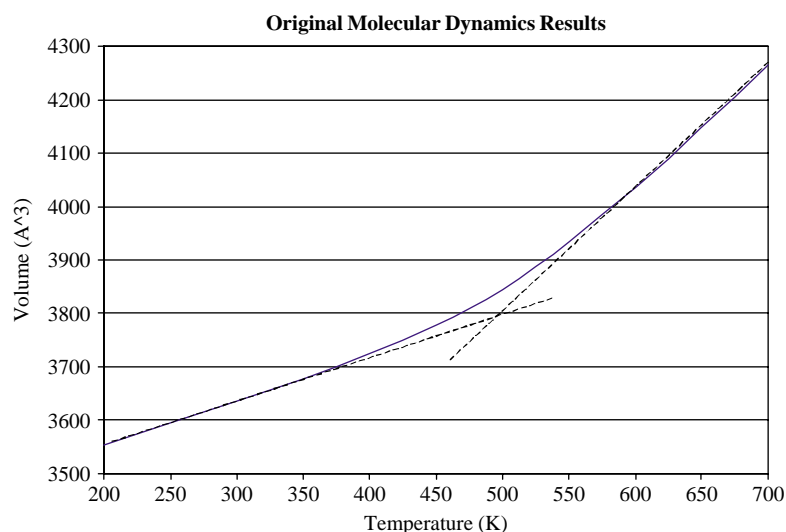

Fig. 2. Initial MD simulation of 'defect-free' poly[bis-4-(4-cyanatophenoxy)phenyl sulphone] showing average cell volume versus simulation temperature (the broken lines are only indicative of the intersection and hence the T_g).

Table 3

Standard deviations at each temperature for the MD simulations performed on the 'defect-free' model for the polycyanurate of bis-4-(4-cyanatophenoxy)-phenyl sulphone

Temperature (K)	200	300	400	500	600	700
Standard deviation	9.57	13.44	21.36	18.69	29.73	38.09

Table 4

Comparison of actual and simulated physico-mechanical parameters for poly[bis-4-(4-cyanatophenoxy)phenyl sulphone]

Physico-mechanical parameters	Simulated value	Experimental value
Density (g cm^{-3})	1.20 (at 0 K)	
	1.31–1.34 (at 300 K)[a]	1.34 (at 298 K)
T_g (K)	510–520	519[b]
		508–528[c]

N/A not measured.

[a] Data derived from simulation experiment performed at 300 K.

[b] Data obtained from DMA in tensile mode at 1 Hz on cured neat resin samples between 123 and 623 K at a heating rate of 5 K min^{-1} (originally published in Ref. [16]).

[c] Data obtained from TMA on cured neat resin samples at a scanning rate of 5 K min^{-1} (originally published in Ref. [16]).

temperatures ranging from 700 to 200 K) were promising and each run took approximately 200 h of CPU time, significantly less than the 1000 h in total previously required [15] (on a smaller machine with a simpler model) using POLYGRAF. The data obtained from these MD experiments are shown in Fig. 2 and the standard deviation in the data at each point are shown in Table 3. The initial analysis suggested that the T_g (as evidenced by the marked change in gradient in the cell volume–temperature plot) lay in the region between 450 and 600 K (a simple extrapolation between these data yielded an intercept above 500 K). However, consideration of these data and the trajectory files of the simulations performed suggested that equilibration had certainly not been achieved at the higher temperatures (600 and 700 K) although there had been a levelling off of volume change at the lower temperatures (Table 4).

Consequently, a longer simulation (lasting 1250 ps) was carried out solely on the 600 K structure using the final structure from the 700 K simulation as the starting point for the new simulation to reproduce the original experiment as accurately as possible. In order to clarify the point at which the discontinuity in the cell volume data occurred, three additional experiments were performed at 560, 520 and 510 K (performed in descending temperature order) using the original 600 K MD simulation as the starting point for these new simulations. Examination of two of the trajectory files demonstrates the greater degree of equilibration achieved
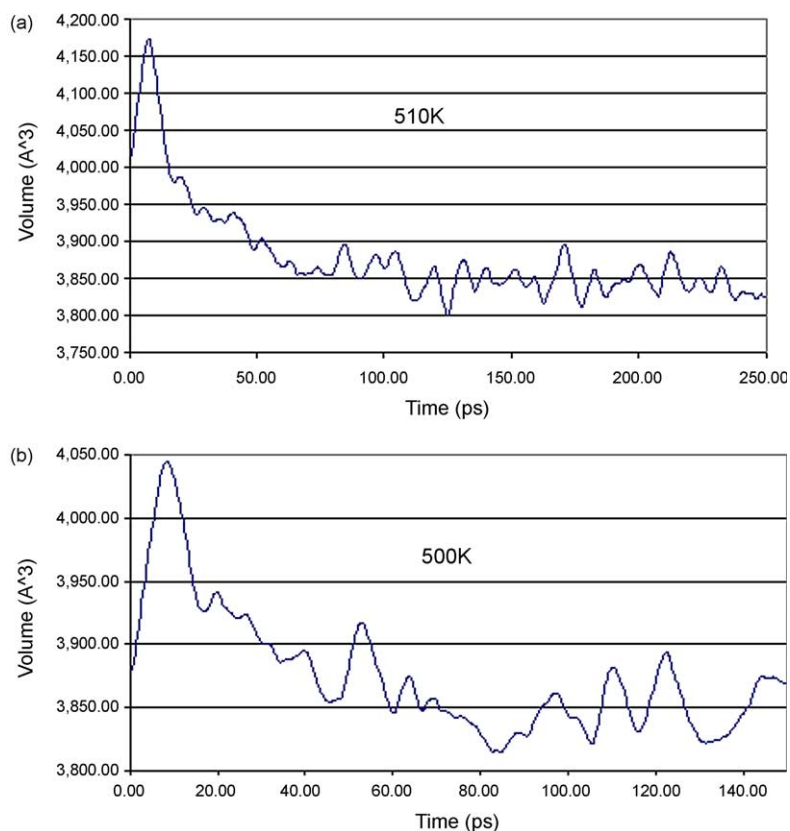

Fig. 3. Trajectory files for the MD simulations performed at (from top) 510 K (150 ps) and 500 K (250 ps) for 'defect-free' poly[bis-4-(4-cyanatophenoxy)phenyl sulphone] showing average cell volume versus simulation time.
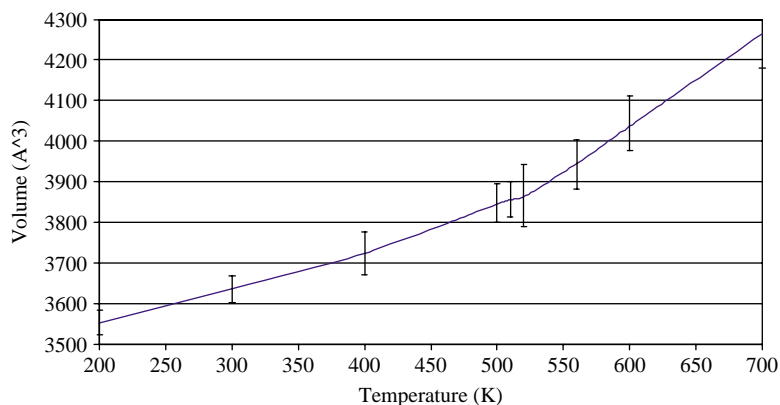
Fig. 4. Final MD simulations of 'defect-free' poly[bis-4-(4-cyanatophenoxy)phenyl sulphone] showing average cell volume versus simulation temperature (dashed lines indicate limits of T_g determined for this material using TMA).

(Fig. 3). The 600 K (1250 ps) equilibration experiment took approximately one week to perform and the variation in the data remained fairly constant after 200 ps. This suggests that the structure will never achieve full equilibration nor explore a

smaller range of energetic states as, at this temperature, there is a much larger number of conformations (of very similar volume and density and hence equal probability) that the polycyanurate can adopt.

Fig. 4 shows the full data set including the original set of simulations and the subsequent 'interpolation' experiments. The discontinuity appears to lie between 510 and 520 K indicating the apparent glass transition temperature (T_g) of the polymer. An independent study, undertaken in a separate laboratory to determine the empirical T_g for the same cured polycyanurate yielded values of 519 K (using DMA) and 508–528 K (using TMA) in close agreement with the simulation.

Fig. 5 shows the effect of the bulk polymer undergoing the apparent glass transition. In Fig. 5(a), the 27-unit cell 3-d model of poly[bis-4-(4-cyanatophenoxy)phenyl sulphone] is shown as constructed and minimised (prior to MD simulation);
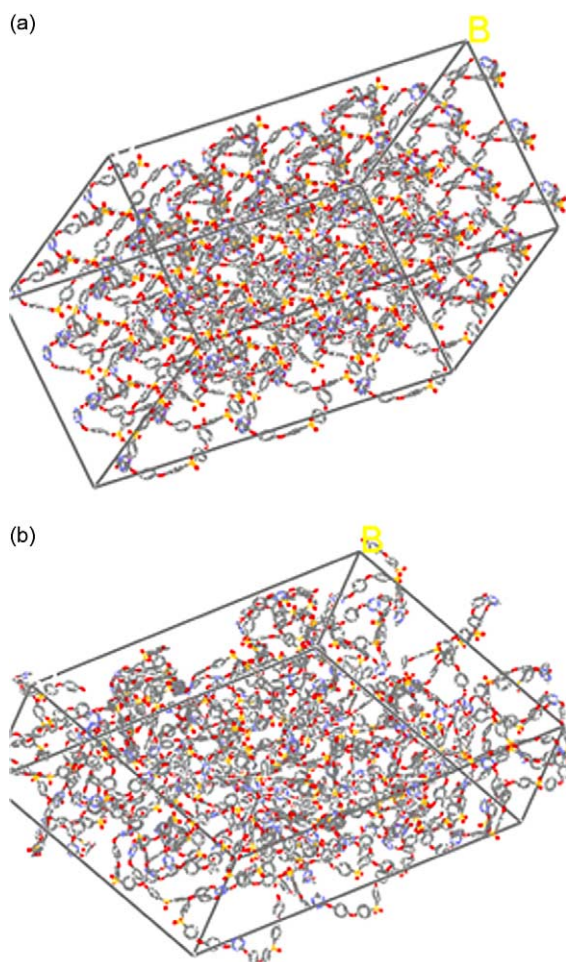

Fig. 5. 27-unit cell 3-d models of 'defect-free' poly[bis-4-(4-cyanato-phenoxy)phenyl sulphone] (a) initial conformation and (b) following the MD simulation at 510 K (NB, oxygen atoms are shown in red, nitrogen atoms in blue, sulphur atoms in yellow, carbon atoms in black and hydrogen atoms in white) (For interpretation of the reference to colour in this legend, the reader is referred to the web version of this article)
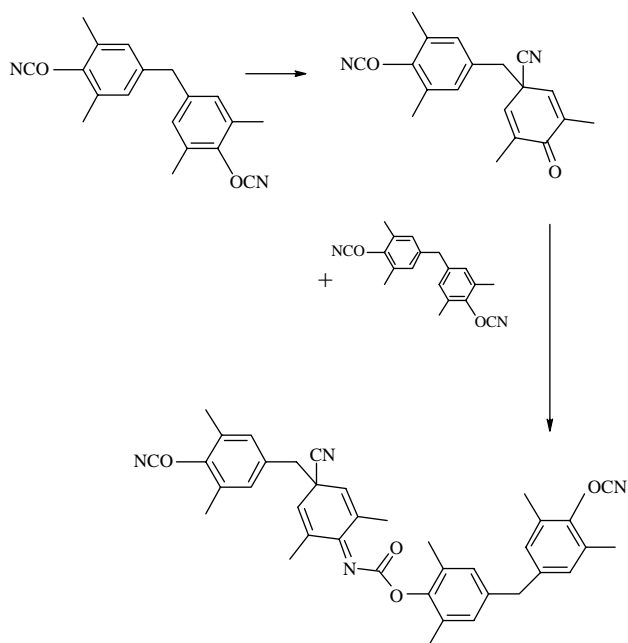
Scheme 2. Reaction pathway postulated to form the structural irregularity (shown for bis(3,5-dimethyl-4-cyanatophenyl)methane, AroCy M). This structure would go on to polycyclotrimerise through the cyanate groups in the normal manner.
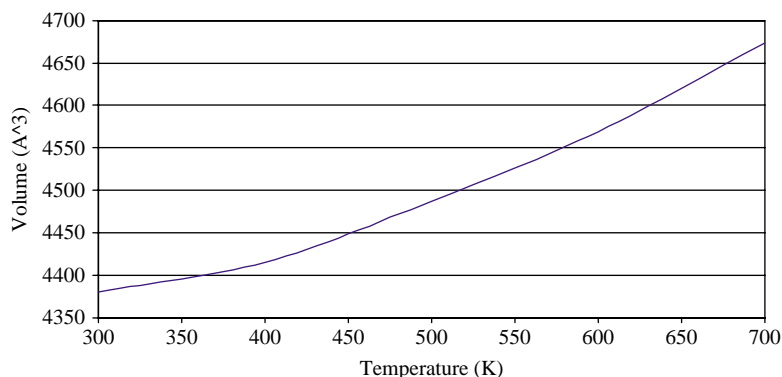
Fig. 6. MD simulations of poly[bis-4-(4-cyanatophenoxy)phenyl sulphone] (containing ca. 5% structural defects) showing average cell volume versus simulation temperature.

Fig. 5(b) represents the same model following the MD simulation at 510 K (after the apparent transition has occurred). The structure demonstrates the increased disorder in the model that is apparent following the MD experiment.

3.3. Effect of structural defects on the predicted T_g

Naturally it is not possible to determine the exact nature and amount of the structural defects in a cured thermoset system. The object of this work was to see if incorporation of a small percentage of defects, thereby making the model less crystalline and slightly more amorphous, would have on the simulated T_g. As expected the T_g falls on their incorporation. The initial simulations were performed using 'perfect' network structures in which every cyanate group was assumed to undergo reaction and also to contribute to the formation of a three-dimensional network. However, in reality this is rarely achieved as most polycyanurates develop 'structural defects' during the cure process. Bauer et al. [23] have reported the results of a study of the curing behaviour of a commercial dicyanate, bis(3,5-dimethyl-4-cyanatophenyl)methane (otherwise known as AroCyM). They concluded that the occurrence of structural defects (of the form shown in Scheme 2) is particularly a problem when cyclotrimerisation catalysts are used during the cure process, although the generation of these structures was not predictable, nor reproducible. As this may occur during routine processing, it is important that any reliable simulation should be able to accommodate the inclusion of defects in the network stucture. In passing, it should be noted that FT-IR analysis [16] of the cured polycyanurate (from which the empirical data were derived) showed no detectable quantities of the structural defect postulated by Bauer et al. [23] This finding was evidenced by the lack of bands characteristic of the nitrile group—thought to arise from rearrangement of the cyanate group. This indicates that while the polycyanurate is unlikely to be perfect, it is unlikely to contain significant quantities of this structural defect, making the modelled structure a reasonable representation of the real material.

Defects were added randomly to five of the 108 cyanurate rings in the original 27-unit cell model. This would yield a fully converted polycyanurate network containing irregularities in around 5% of the triazine rings in the structure—a similar

figure was determined spectroscopically for AroCy M [23]. The modelling of the defects was not a trivial task since the 27-unit cell is extremely complicated when viewed on screen. Consequently, limited success was achieved in placing the defects randomly through the entire structure and three out of the five defects were placed on the same (most easily accessed 'front') plane. As the actual positioning of the defects (already random and variable) in the polycyanurate is not known, this 'clustering' may not be unrepresentative.

Unfortunately, it has not been possible to measure the T_g for a sample of poly[bis-4-(4-cyanatophenoxy)phenyl sulphone] containing the same number of defects, since their introduction
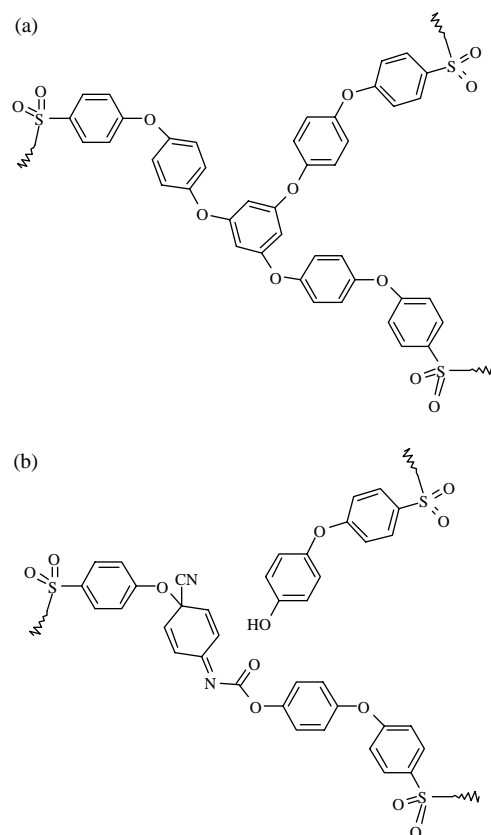
Scheme 3. (a) Portion of 'defect-free' network used in simulation (b) introduction of defect showing residual hydroxyl group on adjacent chain.

is not controllable. However, the trend is a significant drop (of around 70 K) in the value of T_g of a 'perfect' polycyanurate of bis-4-(4-cyanatophenoxy)phenyl sulphone from ca. 520 to ca. 450 K (Fig. 6), along with an accompanying increase in the net cell volume. Both changes are consistent with an increase in the free volume of the system resulting from the introduction of structural defects and, hence, a reduction in the cross-link density. In their empirical study, Bauer et al. [23] found that the polycyanurate of AroCy M underwent a reduction in the value of T_g from ca. 558 K for a 'regular' sample representing a conversion of 96.4% (and negligible irregularity) to 518 K for a sample representing a conversion of 93.8%, containing highly irregular structures (Scheme 3).

4. Conclusions

We do not adjust our T_g values to the experimental conditions, we just compare the simulated T_g values to those determined from experiment. Hence both determinations are independent and unbiased by each other. As the T_g is not a first order thermodynamic transition, its experimentally determined value depends on how it is measured so there is always a range when measured experimentally. We seek to correlate the increase in volume of our system with temperature to the onset of main chain motion in the real system. In our latest paper on the simulation of benzoxazine systems [24] we have added a range for the experimental T_g determinations to the specific volume versus temperature graph and this makes the agreement even better. We have also simulated and published on epoxy resins over the years using this technique albeit in a cruder implementation.

Other papers also published in Polymer have used similar techniques to ours to determine the T_g from molecular simulation, e.g. Pozuelo and Baselga [25], where they studied poly(3-aminopropyl methyl siloxane) and found a T_g of 213 K close to the experimental value. Also Wolfgang Paul [26] has discussed the subject of glass transition simulation in polymer melts using 1,4-polybutadiene as the example. These widely differing structures simulated under similar conditions point to the generality of the simulation technique and the confidence we can have in the results of such simulation.

The results of this study show that it is possible to reproduce the empirical density of this polymer with some accuracy using a large, but regular molecular model. It is also possible to simulate a transition, which can be compared with remarkable accuracy to the empirical T_g Furthermore, it is possible to incorporate the latest evidence on the structural defects in these polymers and simulate the effect that incorporation of a small percentage of these has on the expected physical and mechanical properties of the polymer. The results from these 'defect' simulations are consistent with the drop in T_g found in other polycyanurate systems.

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