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# Conformational studies of polycyanurates: a study of internal stress versus molecular structure

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## Abstract

A new parameter set (RDA-DR.2.21\_Inv) is shown to reproduce both the geometries and the physical and mechanical properties of three polycyanurates based on 2,2-bis(4-cyanatophenyl)propane, 1,1-bis(4-cyanatophenyl)ethane and 1,3-bis(4-cyanatophenyl-1-(1-methylethylidene))benzene. The results show a trend of internal stress within the molecule caused by varying backbone structure. The simulated Young's modulus of elasticity decreases in the order: 1,1-bis(4-cyanatophenyl)ethane > 2,2-bis(4-cyanatophenyl)propane > 1,3-bis(4-cyanatophenyl-1-(1-methylethylidene))benzene (from 31.11 to 14.33 GPa). Molecular dynamics simulations, carried out on 1,1-bis(4-cyanatophenyl)ethane and 1,3-bis(4-cyanatophenyl-1-(1-methylethylidene))benzene, reproduce the empirical glass transition temperatures ( $T_g$ ) of the polycyanurates well, although the calculated  $T_g$  values are slightly overestimated when compared with the empirical data, presumably due to the 'perfect' nature of the simulated network. © 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** Cyanate esters; Polycyanurates; Molecular modelling

## 1. Introduction

With the ever-increasing electronic content in a wide variety of products, from aeroplanes and cars to commonplace household appliances, the world demand for (and dependence on) electronic components is growing. It is predicted that world shipments of electronic components will increase more than 9% per year to reach \$486 billion in 2004 [1]. Furthermore, the world market for electronic chemicals is heavily concentrated in a small group of countries, e.g. North America (principally USA) and Asia (Japan, South Korea and Taiwan) accounted for almost 86% of global demand in 1999 [1]. As electronic devices become increasingly complex and more sophisticated, electronic circuitry is rapidly evolving into smaller, more powerful and faster multi-layer units, comprising sequentially built, thin layers of metallised conductors on ceramic or silicon substrates and unreinforced polymer dielectric films. These multi-chip modules (MCMs) offer the possibility of designing high-density interconnects for mounting chips used in digital processing. However, these devices place

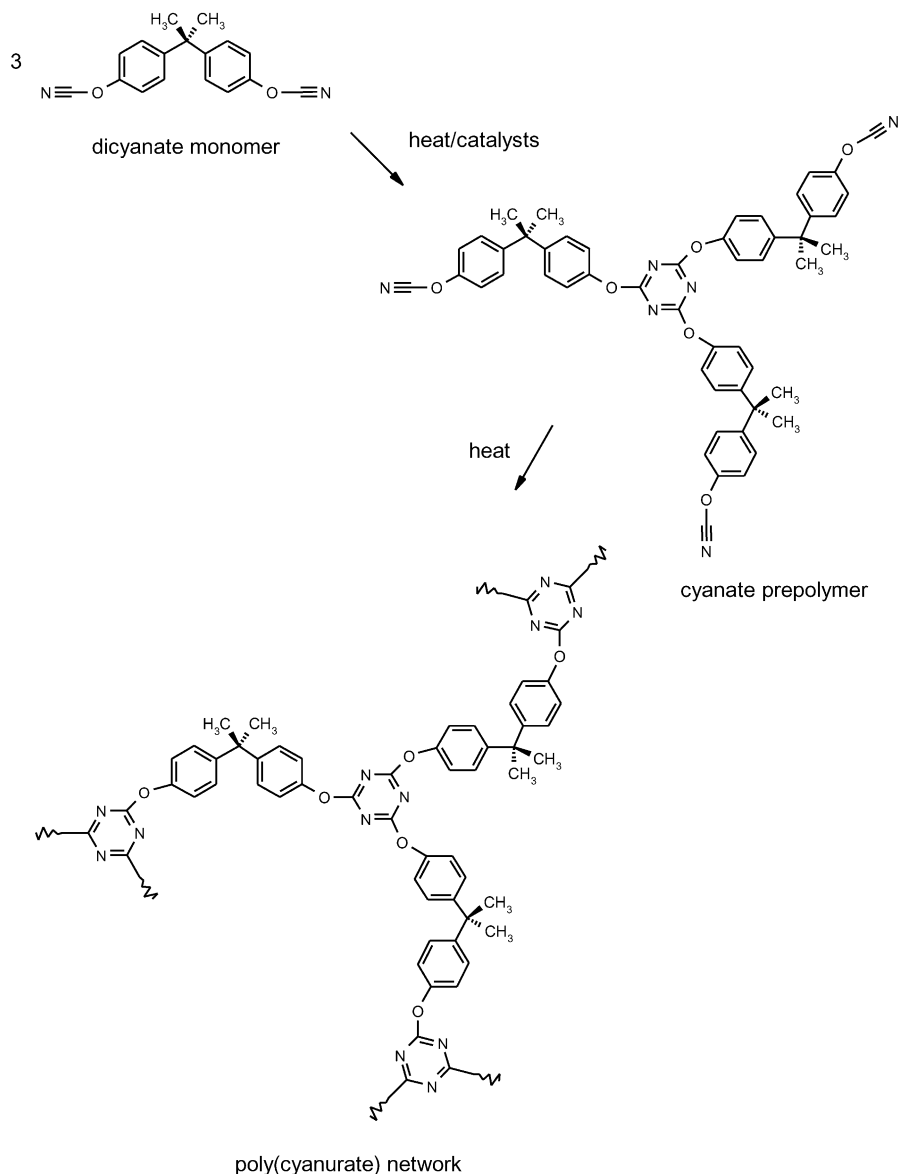
increasing demands on dielectric polymers for both lower dielectric loss properties while maintaining device reliability.

Cyanate ester resins (CEs) are a family of thermosetting resins that are used within a variety of electronic and microelectronic applications. The cyanate monomers offer low toxicity ( $LD_{50} \geq 3$  g/kg), ease of processing and versatile cure and blending options and undergo cure via the formation of cyanurate rings (*sym*-triazine rings linked by aryl ether linkages to a polymer, correctly termed a polycyanurate). A simplified reaction is depicted in [Scheme 1](#) for 2,2-bis(4-cyanatophenyl)propane, available commercially as AroCy B-10. (A range of catalyst packages may be used, but these generally comprise a transition metal carboxylate or chelate and an alkyl phenol.)

Although this reaction scheme predominates, there is also evidence [2] for the formation of cyanurate rings containing either one or two terminal hydroxyl groups (arising from the incorporation of, e.g. 2-(4-cyanatophenyl)-2-(4'-hydroxyphenyl)propane into the growing network—the species arising from partially hydrolysed dicyanate monomer). Furthermore, there has been empirical work undertaken to show the presence of small but significant quantities of triazine bicyclopentane species within cured polycyanurates using secondary ion mass spectrometry [3]

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Scheme 1. Simplified cyclotrimerisation reaction to produce polycyanurate network (shown for 2,2-bis(4-cyanatophenyl)propane).

and high performance liquid chromatography [4]. These are thought to arise from intramolecular reaction of three cyanate monomers to form species that do not contribute to the crosslinked polycyanurate network.

The cured polycyanurates offer high performance, including relatively high glass transition temperature ( $T_g = 190\text{--}290\text{ }^\circ\text{C}$ , depending on structure and degree of cure), high fracture toughness (typically  $G_{IC} = 140\text{--}225\text{ J/m}^2$ , although this can be raised significantly by blending with engineering thermoplastics) and good hot/wet performance [5]. The single largest application for polycyanurates is the use 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 [6]. In fact, the fastest growing use for polycyanurates is in high frequency

units designed for 600–12 GHz wireless communication and tracking systems for, in addition to the general properties already outlined earlier, the polymers also develop interesting dielectric properties that make them particularly attractive in this application, for which epoxy resins and polyimides are market contenders. For instance, cured polycyanurates display low dielectric loss properties (typically, the dielectric constant,  $D_k = 2.2\text{--}2.7$  and dissipation factor,  $D_f = 0.003$  at GHz frequencies) and low moisture absorption (typically less than 3 wt% in short–medium term conditioning studies). In the former case, lower dissipation factors proportionally reduce power loss and heat production in MCMs which, in turn, means that operating speeds are increased, ‘crosstalk’ (the interaction between electrical fields of adjacent electrical conductors) is reduced and dimensional stability is maintained. The importance of maintaining low moisture

absorption is made clearer if one considers that, with a  $D_k$  of 78, the absorption of even quite small quantities of water in thermoset resins can affect their dielectric properties quite markedly.

Generally, polycyanurates offer consistent performance and dimensional stability over wide temperature ranges with exposure to humidity, circuit processing chemicals and corrosive environments, when compared with competitor resins, such as bismaleimides or epoxy resins. Ideally, zero dimensional change should occur during the cure of the dielectric polymer, when heated or cooled during processing or service, and when subjected to environmental fluids and variable humidity conditions. In practice, however, a degree of dimensional change occurs with all polymers (and indeed all materials) and can lead to a number of problems, including delamination and warping. This can be particularly evident in complex electronic packages, where both dielectric polymer and, e.g. a silica substrate may be in direct contact and the delamination and warping may arise due to a mismatch in the coefficients of thermal expansion (CTEs) of the respective materials. For instance, the CTE of a silicon wafer is ca. 3.0 ppm/°C [7], whereas typical commercial polycyanurates develop CTEs between 62 and 71 ppm/°C [8] after cure. The effect of this mismatch is evidenced by the warpage observed in the two layers (the greater the mismatch, the larger the warpage). This can have catastrophic consequences in the production of MCMs and may lead to either delamination of the separate layers or disruption of electrical connections between the components. This leads to a need for a greater understanding of CTE/internal stress in the components used in microelectronics. In this paper, we discuss a molecular modelling approach to one of the components (the dielectric polymer) that has been carried out in order to obtain an understanding of the effect of molecular structure on the internal stress generated during the cure of selected polycyanurates. These materials are known commercial cyanates and this paper is a

part of our continuing academic study on the molecular modelling of network forming synthetic polymers.

## 2. Experimental

### 2.1. Equipment

Molecular simulations of the polycyanurates were performed using a Silicon Graphics 'Indy R4600' workstation running under Irix 6.3 with the Cerius 2 (Molecular Simulation 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 [9], in conjunction with the  $Q_{eq}$  charge calculation [10]. RDA-DR2.21\_Inv was especially parameterised to reproduce the geometry of the *sym*-triazine ring. These parameters lead to the bond distances and angles presented in Table 1 for each of the dicyanates studied.

## 3. Methodology

### 3.1. Molecular mechanics (MM) study

A series of three dicyanate monomers was identified, including two that are available commercially: 2,2-bis(4-cyanatophenyl)propane (AroCy B-10) and 1,1-bis(4-cyanatophenyl)ethane (AroCy L-10) and an 'experimental' monomer 1,3-bis(4-cyanatophenyl)-1-(1-methylethylidene)benzene (XU 366) (Fig. 1).

Initially, a two-dimensional model was constructed (using the 3D builder module) on an atom-to-atom basis using two *sym*-triazine rings to yield a model comprising four bonding points. The original cell was then converted to a primitive superlattice of *P1* symmetry, giving a three-dimensional cell comprising four *sym*-triazine rings and

Table 1  
Bond distances and angles of the *sym*-triazine ring in three commercial polycyanurates obtained using the RDA-DR2.21\_Inv force-field (for the given conformation)

Dicyanate	Bond distances (Å)			Bond angles (°)				
	C–N	O–C	C–O	C–N–C	N–C–N	N–C–O	C–O–C	O–C–C
<i>AroCy L10</i>								
Mean	1.336	1.345	1.363	110.2	125.1	117.4	125.7	118.5
Standard deviation	0.004	0.003	0.003	2.679	1.209	1.728	4.126	1.750
%Standard deviation	0.315	0.243	0.232	2.432	0.967	1.471	3.282	1.477
<i>AroCy B10</i>								
Mean	1.336	1.345	1.365	110.2	125.0	117.5	126.8	118.7
Standard deviation	0.005	0.003	0.003	2.211	1.325	1.792	4.907	2.423
%Standard deviation	0.396	0.195	0.256	2.006	1.059	1.526	3.869	2.044
<i>XU 366</i>								
Mean	1.336	1.346	1.363	110.9	125.0	117.5	126.3	118.4
Standard deviation	0.002	0.003	0.004	1.254	1.020	1.495	2.188	1.277
%Standard deviation	0.173	0.224	0.278	1.131	0.816	1.273	1.733	1.079

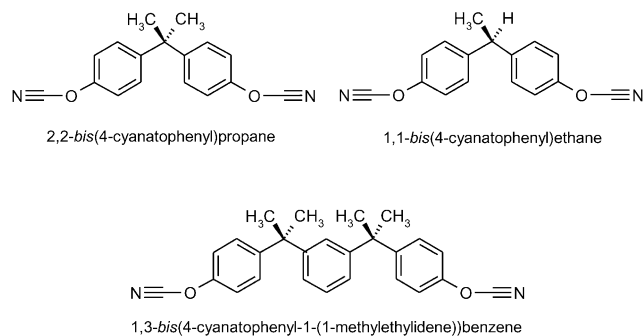


Fig. 1. Structures of dicyanate monomers studied in this work.

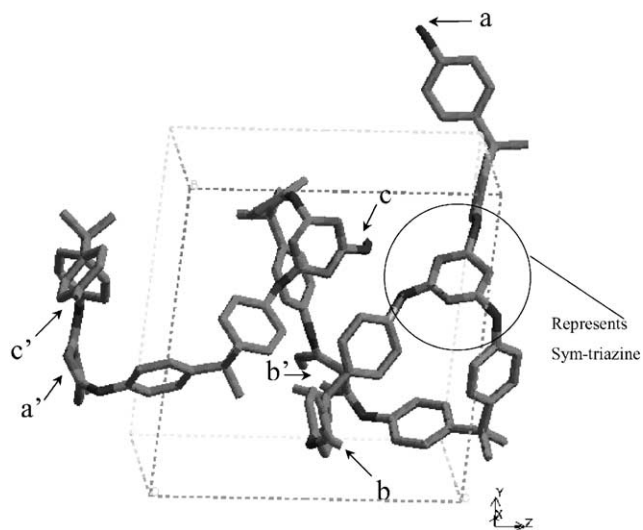


Fig. 2. Unit cell of 2,2-bis(4-cyanatophenyl)propane (AroCy B-10).

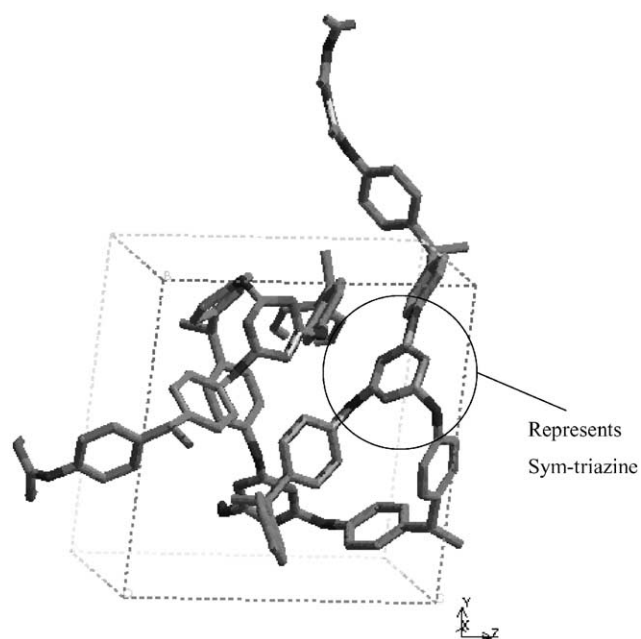


Fig. 3. Unit cell of 1,1-bis(4-cyanatophenyl)ethane (AroCy L-10).

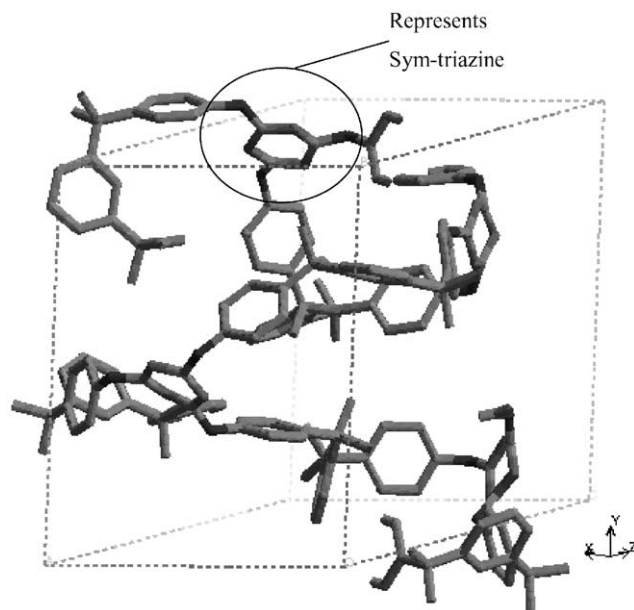
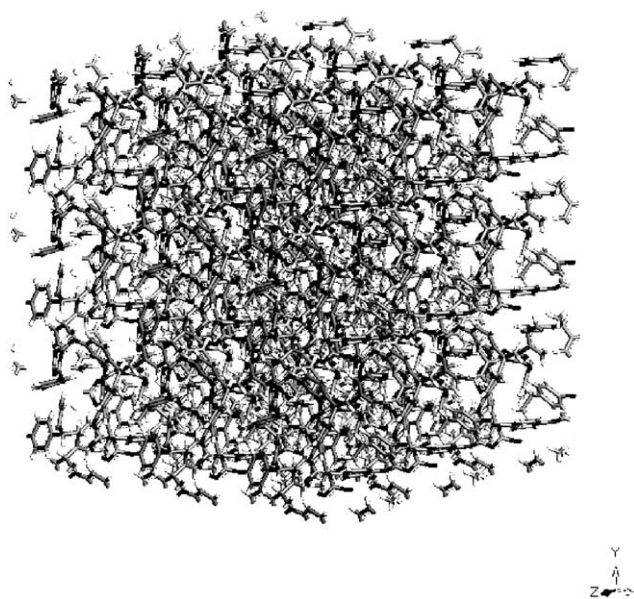


Fig. 4. Unit cell of 1,3-bis(4-cyanatophenyl)-1-(1-methylethylidene)benzene (XU 366).

leaving six bonding points available to extend the structure (Figs. 2–4) by connecting  $a$  to  $a'$ ,  $b$  to  $b'$  and  $c$  to  $c'$ , respectively (shown in figure 2).

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.

Periodic cells were constructed to reproduce the experimental densities (detailed in the appendices of Ref. [4]) and a representative sample is shown for 1,1-bis(4-cyanatophenyl)ethane in Fig. 5. This was the starting point for the energy minimisation in the MM studies.

Fig. 5. Model representing nine periodic cells ( $3 \times 3 \times 3$ ) of 1,1-bis(4-cyanatophenyl)ethane (AroCy L-10).

Density, volume and cell dimensions, relative energies and internal stress were calculated for each molecule.

### 3.2. Molecular dynamics (MD) study

The MD module in Cerius 2 [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 50 ps or 50,000 simulation steps. Simulations were initially conducted at 0 K and thereafter at 100 K intervals up to a maximum of 1000 K. The changes in cell volume were plotted using volume thermal expansion coefficient (VTEC)— $d(V - V_0)/dV$  against a working range of temperature, typically 300–800 K. A linear fit was made to the plot and the intercept between the linear plot and the point of greatest step increase in volume gave the  $T_g$  of the polymer.

## 4. 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 us involving molecular modelling of polycyanurates [11,12] as well as some studies of network build up in the same polymers conducted by other researchers [13,14]. As part of our continuing studies into the molecular modelling of these species we report here a study of the effect of varying the backbone structure of the resulting polycyanurate, whilst simultaneously energy minimising to effectively zero internal stress. The ultimate aim is to investigate the resulting predicted physical and mechanical properties to decide whether molecular design of the backbone structure is feasible and to this end we have studied three commercially available materials. This work continues and in a future paper we will address the question of property prediction. Naturally, 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.

### 4.1. Molecular mechanics data

The unit cell data (derived from Cerius 2) for all the polycyanurates are given in Table 2. In order to compare the structures at stress free values, all the models were optimised to an internal and external stress of 0 GPa. An examination of the backbone structure of the models reveals that we are studying the effect of increasing complexity of the linkage group between the two phenyl rings in the side chain of the resulting polymer. As the complexity of the backbone increases the possible degrees of freedom for packing of the molecule in the cell increases and the

Table 2

Summary of data derived from Cerius 2 experiments for three dicyanates (for a given structural conformation)

Cell parameters	Dicyanate		
	AroCy L10	AroCy B10	XU 366
Density (g/cm <sup>3</sup> )	1.18	1.13	1.04
Volume (Å <sup>3</sup> )	2222.28	2452.57	3785.10
<i>Dimensions (Å)</i>			
<i>a</i>	12.41	12.51	14.21
<i>b</i>	13.93	14.26	15.96
<i>c</i>	13.15	13.86	16.83
<i>Angles (°)</i>			
$\alpha$	84.46	84.17	87.46
$\beta$	99.27	93.20	91.18
$\gamma$	96.88	92.67	96.80
<i>Optimised repeat cell</i>			
Relative energy (kcal/mol)	166.56	296.26	688.81
RMS force ((kcal/mol)/Å)	0.004	0.004	0.004
Internal stress (GPa)	0.000	0.000	0.000
<i>Mechanical properties</i>			
Bulk modulus (GPa)	24.51	18.39	10.15
Compressibility (GPa)	0.041	0.054	0.099
Young's modulus (GPa)	31.11	23.96	14.33
Poisson ratio	0.298	0.311	0.273
Lamé constant, $\lambda$ (GPa)	15.357	12.766	8.257

calculated density goes down. This is apparent from Table 1 where the calculated density for 1,1-bis(4-cyanatophenyl)ethane (AroCy L-10) is 1.18 g/cm<sup>3</sup> and for 2,2-bis(4-cyanatophenyl)propane (AroCy B-10) is 1.13 g/cm<sup>3</sup>. 1,3-bis(4-cyanatophenyl-1-(1-methylethylidene))benzene (XU 366) has the most complicated backbone of the compounds studied and therefore has the lowest calculated density of 1.04 g/cm<sup>3</sup>.

The simulated Young's modulus of elasticity decreases in the order, 1,1-bis(4-cyanatophenyl)ethane to 2,2-bis(4-cyanatophenyl)propane to 1,3-bis(4-cyanatophenyl-1-(1-methylethylidene))benzene, from 31.11 to 14.33 GPa and hence reflects the nature of the backbone: whereby the degree of substitution and complexity increases in the same manner.

### 4.2. Molecular dynamics data

MD simulations were carried out on both 1,1-bis(4-cyanatophenyl)ethane and 1,3-bis(4-cyanatophenyl-1-(1-methylethylidene))benzene in order to calculate the  $T_g$  of the commercial polycyanurates AroCy L-10 and XU 366, respectively. The MD data for 1,1-bis(4-cyanatophenyl)ethane are shown in Fig. 6.

The results from the simulations gave values that were comparable with empirical data obtained for the cured commercial polymers (Table 3). However, in both cases the simulation model overestimated the  $T_g$ , although

Table 3  
Comparison of actual and simulated glass transition temperatures in polycyanurates

Polycyanurate	Glass transition temperature, $T_g$ /°C (K)	
	Experimental value	Simulated value
AroCy L-10	258 (532)	264 (537)
XU 366	192 (465)	246 (519)

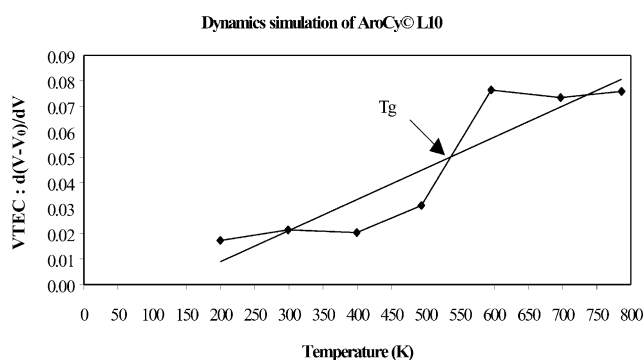


Fig. 6. Dynamic simulation of 1,1-bis(4-cyanatophenyl)ethane (AroCy L-10).  $V_0$  = initial cell volume,  $dV$  = change in cell volume.

the agreement with AroCy L-10 (1,1-bis(4-cyanatophenyl)ethane) appears to be remarkably good. This overestimation is likely to be a result of the perfect nature of the model (i.e. lacking molecular defects or bulk microcracks or voids and representing a fully converted polycyanurate containing no residual monomer or intramolecular cycles). As mentioned previously, the latter have been postulated [3] to form in small quantities during the polymerisation reaction and are not included in the perfect models considered here.

As would be expected, the more flexible backbone of the XU 366 molecule (1,3-bis(4-cyanatophenyl)-1-(1-methyl-ethylidene)benzene) results in a lower simulated  $T_g$  value. This represents the lower amount of energy required to initiate main chain motion in the polymer in XU 366 than in the case of the AroCy L-10 molecule. Hence, an indication of softening temperature can be arrived at from a study of a comparative series of molecules and can therefore be used as an aid to the design of polymers tailored for specific applications.

## 5. Conclusions

The parameter set designated RDA-DR2.21\_Inv is able to reproduce both the geometries and the physical and mechanical properties of three commercial polycyanurates. The results may be interpreted in terms of internal stress within the molecule caused by varying backbone structure and allow rationalisation of both the Young's modulus of elasticity and the  $T_g$  for two selected molecules. This should allow the prediction of the physical and mechanical properties of new potential polycyanurates prior to synthesis for future technological application, particularly within the microelectronic and aerospace industries.

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