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A Molecular Dynamic Simulation of Crosslinking of Bisphenol and Triazine by United Atom Model: A Polycyanurate Model

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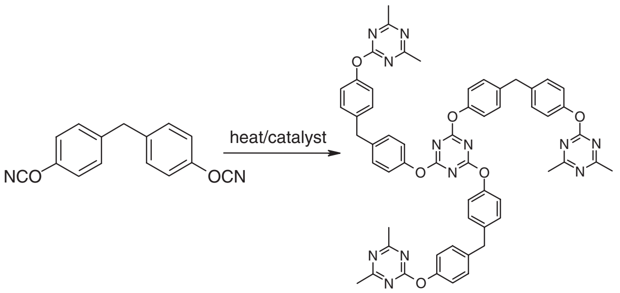
Polycyanurate networks were densely built by crosslinking of bisphenols and triazine. A molecular dynamics study of the networks from bisphenol A, bisphenol E, and fluorene bisphenol qualitatively reproduced the glass-transition temperatures in correct orders.

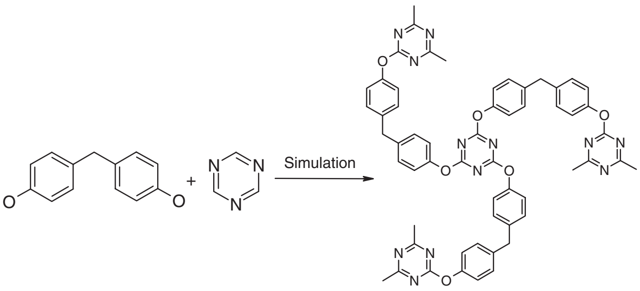
Cyanate resins (polycyanurates) are one of groups of well-known thermosetting polymers. Compared to epoxy resins, they have relatively high glass-transition temperatures (T_g), high heat resistance, low dielectric constants, low dissipation factors, and high radiation resistance.[1] Hence, they are used where epoxy resins cannot achieve desired properties. Printed circuit board in electronics is one successful application of cyanate resins and, for example, BT (bismaleimide triazine) resins composed of bismaleimides and cyanates have been widely used.[2] In this area, various requirements of new cyanates that satisfy fire retardance, lead-free soldering ability, high heat resistance, low warpage, low moisture absorbency, and so on, have increased year by year. In order to design cyanate monomers effectively, computer simulations may become powerful tools, and the number of papers related to molecular dynamic simulations of the cyanate resin and other thermosetting polymers has increased.[3–5] Howlin and co-workers have widely studied the molecular simulations of cyanate resin.[3] They developed a force field for polycyanurates[3c] and built a no-defect 3D cyanate resin structure by connecting a 2D model regularly and reproduced the T_g and other physical properties.[3a,3b] On the other hand, molecular simulations of the crosslinkage of epoxy have been intensively studied recently.[5] The structure of epoxy resin has been built from an epoxy monomer and a hardener by molecular dynamic simulation, and various physical properties have been calculated from the obtained network. And furthermore, the method was applied to more complex systems, such as nanocomposites[5c,5h] and absorbed water influence.[5f,5i] Accordingly, it was considered that the crosslinking method should also be useful with polycyanurates, but as far as we know, it has not been well applied. In this communication, we report the crosslinking study of bisphenols and triazine as a cyanate resin model and the molecular dynamic simulations of some thermal properties.

OCTA2006 revision 3, developed by the Doi group,[6] and its user-friendly version J-OCTA 1.4[7] were used as programs for the molecular dynamic simulations.

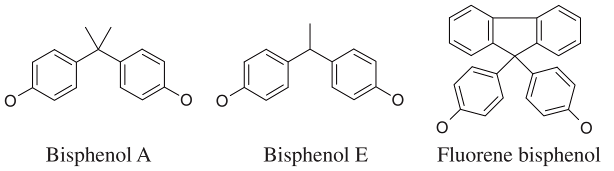
A cyanate resin was thermally cured through the trimerization of a cyanate monomer, usually in the presence of a catalyst, such as zinc octate (Scheme 1). The mechanism of the triazine formation has been disputed and is complex.[8] For example, a stepwise mechanism was proposed by theoretical calculation.[8c] Because the stepwise mechanism, even the simulation of the concerted mechanism seemed cumbersome, a simpler model reaction was adopted. The C–O bond formation of a bisphenol and triazine was considered as shown in Scheme 2. When the oxygen atom of the bisphenol and the carbon atom of the triazine ring came close, the C–O bond was set to be formed. If C–O bonds were completely formed, it became the perfect model of polycyanurate.[3a,3b] On the contrary, when they were not completely formed, the remaining units were different from the real polycyanurates. However, if the ratio of the C–O bond formation was sufficiently high, it was thought that the physical properties and T_g should not be so different from the real system and that it could be used for comparison.



Scheme 1. Polymerization of cyanate.

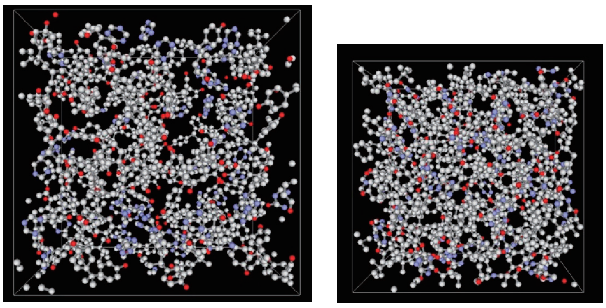


Scheme 2. Model reaction for MD simulation.


Bisphenol A Bisphenol E Fluorene bisphenol

Scheme 3. Examined bisphenols (hydrogen atoms were omitted for calculation).

Bisphenol A, bisphenol E, and fluorene bisphenol were chosen as representative bisphenols (Scheme 3). The united atom model and the Dreiding force field embedded in J-OCTA were used by default.[9] Electronic effects were not considered throughout the simulation.[10] First, an amorphous structure of 90 molecules of bisphenol A and 60 molecules of triazine was



Initial structure
($d = 0.68$ gcm^{-3})

Final structure (500 ps)
($d = 1.05$ gcm^{-3})

Figure 1. Crosslinking structures between bisphenol A and triazine at 800 K (C white; O red; N blue).

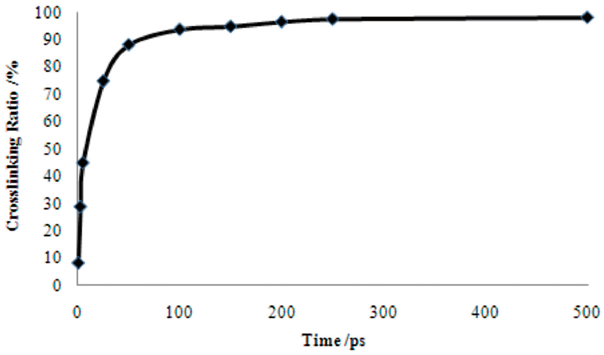


Figure 2. Time course of crosslinking of bisphenol A and triazine at 800 K.

calculated in the NPT ensemble at 800 K.[11] A Nose–Hoover thermostat and an Andersen–Hoover barostat were used to control the temperature and the pressure, respectively.[12–14] The crosslinking simulations were then performed under periodic boundary conditions at 500 and 800 K at 1 atm for 500 ps (time step = 1 fs, total 500000 steps).[15] It was judged every 0.5 ps and if the oxygen atom of the bisphenol and the carbon atom of triazine were within 3.5 Å,[16] the bond was set to be formed and new Dreiding force field parameters were assigned. By the assignment of new parameters at every bond-forming step, internal stress would be reduced.[5b,17] The structures and density before and after the crosslinking simulation at 800 K are shown in Figure 1, and the time course of the bond-forming ratio is shown in Figure 2.[18] As the reaction proceeded, the density increased from 0.68 to 1.05 g cm^{-3}. Half of the C–O bonds were made within the initial 5 ps, and then the ratio gradually increased to 98.3%. This indicated that 177 bonds in 180 possibilities were formed and that there was no unrealistic structure. On the basis of this, it was concluded that the simulation produced a sufficient model of the cyanate resin structure for qualitative analysis. Bisphenol E and fluorene bisphenol were similarly calculated and the results are summarized in Table 1. The bond formation of bisphenol E was slightly faster than that of bisphenol A, but the final crosslinking ratio was similar. In contrast, that of fluorene bisphenol was slower, and the final ratio was lower due to the steric reason.

Next, T_g was calculated from the crosslinked structures in the NPT ensemble. Nose–Hoover and Parrinello–Rahman methods were used to control the temperature and the pressure, respectively.[13,14,19] After the crosslinked structures were relaxed for 6–10 ns at 800 K (850 K for fluorene bisphenol) at 1 atm, the relaxation was performed at every 10 degrees from 800 to 300 K (from 850 to 300 K for fluorene bisphenol) for 1–3 ns. The calculation error in the rubbery region was large, and it did not converge well near T_g. Therefore, it needed some recalculation to obtain a predictable temperature–specific volume relation. The tendency was stronger when the structure was more crosslinked, and a predictable one was not obtained for the simulation of the 93.3% crosslinking structure of fluorene bisphenol and triazine. The temperature dependence of the specific volume of bisphenol A (crosslinking ratio 92.2%) is shown in Figure 3 as a representative,[20] and the summary of T_g (calculated and experimental) and calculated coefficient of linear thermal expansion (CLTE) are shown in Table 2. The calculated density of polycyanurates from bisphenol A and bisphenol E were 1.19 g cm^{-3} and 1.20 g cm^{-3} at 300 K, respectively.[3b] Both crosslinking ratios gave the same density. All the calculated T_g's were higher than the experimental values, probably due to the cooling rate in the simulation, the difference in the crosslinking ratio between the experiment and simulation, or insufficiency of the parameters and the united atom model.[5c,22]

However, the graph figures for the same bisphenol in different crosslinking ratios were similar, and the experimental

Table 1. Results of the crosslinking simulation

Model[a]	Temperature/K	Ratio/%
BisA 90:Triazine 60	500	92.2
BisA 90:Triazine 60	800	98.3
BisE 90:Triazine 60	500	93.9
BisE 90:Triazine 60	800	97.8
FL 45:Triazine 30	500	87.8
FL 45:Triazine 30	800	93.3

[a] Bis A 90: bisphenol A 90 molecules in a unit cell, Triazine 60: triazine 60 molecules in a unit cell, Bis E 90: bisphenol E 90 molecules in a unit cell, FL 45: fluorene bisphenol 45 molecules in a unit cell, and Triazine 30: triazine 30 molecules in a unit cell.

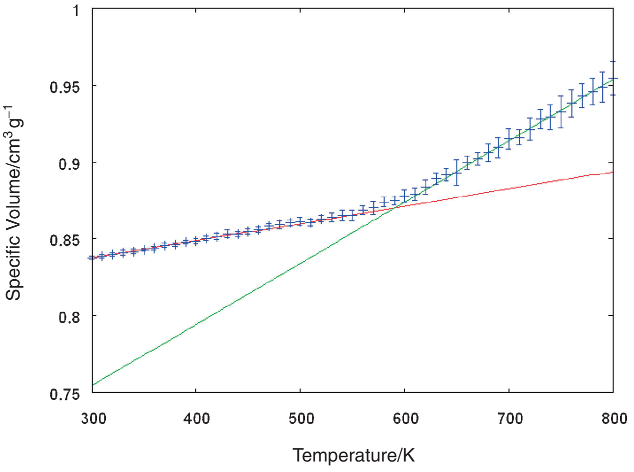


Figure 3. T_g calculation of bisphenol A + triazine (crosslinking ratio 92.2%).

Table 2. Calculated thermal properties

Bisphenol	Crosslinking ratio/%	Calc T_g /°C	Exp T_g /°C[21]	CLTE[a)] /ppm K^{-1}
Bisphenol A	92.2	317	289	44
	98.3	321		41
Bisphenol E	93.9	290	258	56
	97.8	289		47
Fluorein bisphenol	87.8	384	379	41
	93.3	—		—

[a] Calculated CLTE in the glassy region around 300 K.

T_g relation of the bisphenols (T_g(bisphenol E) < T_g(bisphenol A) < T_g(fluorene bisphenol)) was correctly reproduced. Hence, it could be concluded that the method was useful for T_g prediction. The coefficients of volume thermal expansion (CVTE) were calculated from the graphs, and CLTE was obtained by making CVTE one third. The calculated CLTE around 300 K was 41–56 ppm K^{-1}. It was reported that the typical commercial CLTE of polycyanurates was 62–70 ppm K^{-1}.[3b] Accordingly, the calculated values were slightly lower than the experimental, as seen in the simulation of epoxy resin.[5b]

In summary, the application of a crosslinking model to polycyanurates was shown in the model reaction, and it could qualitatively predict T_g and CLTE. A larger system, a longer simulation time, a more realistic model, and an atomistic molecular model might improve the prediction. However, it shows potential to analyze not only cyanate resin but also mixed systems, such as several cyanate blends, cyanate with moisture, BT resins, cyanate–epoxy resins, cyanate–thermopolymers, and composites.

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17 In this simulation, after the assignment of new Dreiding force field parameters, MM relaxation was performed and then the previous velocity was restored. It was confirmed that the amorphous structures used for the T_g calculations did not have any internal strain.

18 The other time-course graphs are shown in the Supporting Information.[23]

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