Study of cyclization reaction pathway of cyanate resin with catalysts by quantum chemical calculation

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Introduction: Next-generation aerospace materials request high-performance properties such as a high glass transition temperature for high-temperature service and strong environmental resistance to adverse working conditions. Cyanate resins, a series of critical functional materials, are used in aerospace materials as matrices according to excellent chemical and physical properties [1]. The network structure controls the properties of cyanate resins, but the relationship between physical structure and properties is still covered. Multiscale simulation, combining the quantum chemistry calculation for energy of reaction barriers and molecular dynamics (MD) simulation with the reaction probability according to the reaction pathway, is one of the ideal approaches to investigate the relationship between properties and structure. Therefore, creating an accurate reaction pathway model by quantum chemistry theory is critical. To achieve that, the global reaction route map (GRRM) program has been used.

Theoretical method: The reaction process was explored by the sphere contraction walk (SCW) and two-point-SHS (2PSHS) approaches in the GRRM program [2]. The bisphenol A dicyanate (BPACN) molecules and the water molecules are the reactant and the catalysts, respectively. The calculation level was RHF/3-21G, and zero-point energy correction was considered.

Result and Discussion: Figure 1 shows the reaction pathway of three molecules of BPACN catalyzed by a water molecule to form a six-membered ring as indicated in a previous study [3]. The energy criterion is three times the energy of one molecule of BPACN plus one water molecule. The energy of the primordial system of the reaction is stabilized by the attractive interactions between the molecules.

There are two stages in this reaction process. First, two cyanate molecules form a four-membered ring containing a water molecule, with an activation energy of about 66 kcal/mol. Second, this four-membered ring reacts with another cyanate molecule to form a six-membered ring that does not contain water molecules. The activation energy for this step is about 80 kcal/mol. In this reaction process, the addition of water molecules to the reaction system produces energetically stable intermediates, but the activation energy of the final step is high and the formation efficiency of cyanate resin may not be very high.

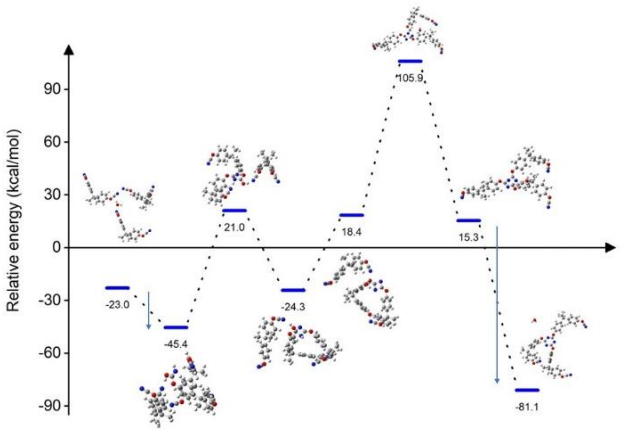

Figure 1. Reaction pathway for cyanate cyclization with water molecule as catalyst obtained by the GRRM program.

References

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