An insight into the polymerization of glycidol with $B(C_6F_5)_3$: DFT calculations of the dimerization reactions

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The polymerization of glycidol (Gly) using tris-(pentafluorophenyl)borane [$B(C_6F_5)_3$] as a catalyst has been recently studied due to the promising results in generating cyclic polymers [1]. The mechanism of polymerization is complex as it involves competitive reactions between [$B(C_6F_5)_3$] and two reactive groups of Gly and between the latter and active centers in the growing chain. The combination of experimental techniques with quantum calculations can lead to a better understanding of this complex process and ideally, to a guide for future polymerization reactions. In present work, DFT calculations showed that interactions between $B(C_6F_5)_3$ and both reactive groups of Gly, the epoxide and hydroxyl, are energetically favored leading to structures B and C, respectively, during initiation (Fig. 1a). Then, the attack of a second Gly monomer on B and C can occur at the methine and methylene carbons of epoxide (reactions “a” and “b”, respectively) leading to a total of 8 possible dimerization reactions at initial states of the propagation reactions (Fig. 1b). Energetic considerations in the DFT calculations clearly showed that only 3 of the 8 reactions are favored. The calculations were performed with the Gaussian 16 program, using the TPSS hybrid functional, triple zeta basis functions (TZVP) and incorporating the contribution of the third order dispersion (GD3BJ).

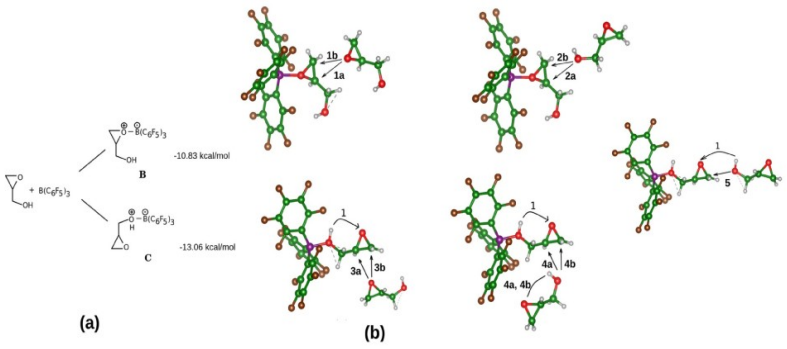

Fig. 1. (a) Initiation: Gly monomer reacting with $B(C_6F_5)_3$ catalyst. (b) Propagation: possible dimerization reactions of Gly. In the figure, Carbon, Oxygen, Boron, Fluorine, and Hydrogen are green , red, violet, brown and gray, respectively.

Reference:

[1] M. A. Al Assiri, E. Gómez Urreizti, C. A. Pagnacco, E. Gónzalez de San Román, F. Barroso-Bujans, European Polymer Journal 171, 11119417, 2022