Computational study of the glycolitic degradation of poly(ethylene terephthalate) catalized by N^1,N^2-bis(2-aminobenzyl)-1,2-diaminoethane zinc(II)

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Abstract

A possible reaction mechanism of the glycolytic degradation of poly(ethylene terephthalate) (PET) catalyzed with N^1,N^2-bis(2-aminobenzyl)-1,2-diaminoethane zinc(II)-(ABEN) was determined using KS-DFT using the meta-NGA hybrid functional, MN15-L[1] up to def2-SVP level of theory making use of an energy-weighted climbing image nudged elastic band (EW-CI-NEB) algorithm[2] to determine the minimum energy path (MEP) and then optimizing the converged climbing image (CI) using eigenvector-following partitioned rational function optimization (EF P-RFO) to obtain the transition state (TS).

Introduction

By 2015, the annual global production of plastics surpassed 367 million tonnes; 55 % of all plastic waste was discarded, 25.5 % incinerated and just 19.5 % was recycled.[3] Poly(ethylene terephthalate) (PET) is one of the most widely used thermoplastics in the packaging and textile industry; due to its increasing overconsumption and non-biodegradablity, it has become a serious environmental problem. Over the last decades, there have been numerous studies on the topic of polymer recycling; by far, the most acceptable method according to the principles of *sustainable development* is the tertiary recycling, or more commonly referred as *chemical recycling,* because it forms *de novo* the monomer(s) involved on the production of the polymer itself or derivatives thereof.[4]

For the chemical recycling of PET, there have been numerous studies involving hydrolysis, methanolysis and glycolysis among many others.[5–7] The uncatalyzed glycolysis of PET is not an effective process; transition metal salts have been determined to aid in this reaction; some zinc salts are great catalysts with the added advantage that their toxicity is diminished.

Methods

The starting configurations for EG and ABEN where proposed and optimized using XTB[8] with the force field GFN2-xTB.[9] The staring configuration for DBHET was proposed using crystallographic data.[10]

The software ORCA (5.0.1)[11] was used to perform the geometrical optimization of the species involved in the depolymerization; PET dimer (DBHET), ABEN and EG in KS-DFT using a meta-NGA functional, MN15-L[1] with the def2-TZVP BS and employing the option to use automatic auxiliary basis set generation.[12]

The optimized structures where then merged onto the same Cartesian coordinates and then re-optimized in MN15-L/def2-SVP Then, a multidimensional relaxed surface scan was performed keeping constrained, and varying the bond distances in 5 steps to obtain the products of this reaction. The optimized product and the starting geometry

of the relaxed surface scan where the input for an Energy-Weighted Nudged Elastic Band (EW-NEB)[2] algorithm to find the path of minimum energy connecting both ends, followed by a P-RFO optimization to find a TS was performed onto the image with the highest energy alongside the MEP.

In order to determine interactions regions between the molecules, an IRI algorithm within multiwfn was utilized[13] with the wavefunctions generated in the previous step.

Using JANPA,[14] CLPOs and the bond orders for the reactants, products and transition states where obtained from the density functional generated by ORCA.

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