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

Pablo E. Alanis González,[*,†,¶] Isabel del Carmen Saenz Tavera,[‡,¶] and Victor Manuel Rosas García[‡,¶]

†*Universidad Autónoma de Nuevo León, San Nicolás de los Garza, N.L.*

‡*Facultad de Ciencias Químicas, Universidad Autónoma de Nuevo León, San Nicolás de los Garza, N.L.*

¶*Facultad de Ciencias Químicas, UANL*

E-mail: pabloalanis1998@gmail.com

Phone: +52 (81) 1177 3600

Abstract

A possible reaction mechanism of the glycolytic degradation of poly(ethylene tereph-thalate) (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 global-hybrid functional, MN15[1] up to def2-SVP/def2-TZVP level of theory making use of an energy-weighted climbing image nudged elastic band (EW-CI-NEB) algorithm[2] to determine the min-imum 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). The non-covalent interactions where obtained using

and averaged independent gradient model (aIGM) algorithm[3]

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.[4] 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, commonly referred as *chemical recycling,* because it forms *de novo* the monomer(s) involved on the production of the polymer itself or derivatives thereof.[5]

For the chemical recycling of PET, numerous protocols involving hydrolysis, methanolysis and glycolysis among many others[6–8] have been reported. The uncatalyzed glycolysis of PET is not an effective process; transition metal (TM) salts have been determined to aid in this reaction. The oldest report of the catalyzed glycolytic degradation of PET was reported by Vaidya and Nadkarni in 1988[9] in which they carried the reaction using different metal acetates as catalysts. Then it was determined that Zn^{II} has a great in comparison to other TM (Mn^{II}, Co^{II} and Pb^{II}) activity as a catalyst in the glycolysis of PET.[10] Alongside the numerous zinc catalysts studied to date, a novel zinc complex made with a polyaza macroligand, N^1,N^2-bis(2-aminobenzyl)-1,2-diaminoethane zinc(II) (ABEN)[11] has shown to have a great catalytic activity in the glycolytic degradation of PET.[12] The main purpose of this article is to evaluate the possible reaction mechanism involved in this catalyzed glycolytic depolymerization of PET with ABEN and determine the covalent or non-covalent interactions involved.

Methods

The starting configurations for EG and ABEN where proposed and optimized using XTB[13] with the force field GFN2-xTB.[14] The staring configuration for DBHET was proposed using crystallographic data.[15]

The software ORCA $(5.0.1)$[16] was used to perform the geometrical optimization of the species involved in the depolymerization; DBHET, ABEN and EG in KS-DFT using a meta-NGA functional, MN15[1] using the def2-TZVP basis set (BS)

The optimized structures where then merged onto the same Cartesian coordinates and then re-optimized in MN15/def2-TZVP. 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 Climbing image Nudged Elastic Band (EW-CI-NEB)[2] algorithm to find the path of minimum energy connecting both ends, followed by a P-RFO optimization to find a TS performed onto the climing image (CI).

In order to determine covalent and non-covalent interactions regions between the molecules, an analysis based on Hirshfeld partition of molecular density (IGMH) algorithm within multiwfn was performed[17] onto the optimized reactant. To minimize computation time, aIGM was performed with the MEP obtained by NEB-TS.

With JANPA,[18] CLPOs and bond orders for the reactants, products and transition states where obtained.

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